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August 1962

## DEVELOPMENT OF MANUFACTURING METHODS FOR GLASS FLAKE REINFORCED PLASTICS

J. J. Aclin  
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A. D. Snyder

**OLIN MATHIESON CHEMICAL CORPORATION**

New Haven, Connecticut  
Contract AF 33(600)-41885

ASD Project 7-788

Final Technical Engineering Report  
8 October 1960 - 7 June 1962

Prototype production processes have been demonstrated feasible for preparation of glass flake resin premixes and subsequent fabrication of parts by compression molding, transfer molding, calendaring and centrifugal casting.

**CHEMICAL ENGINEERING BRANCH  
MANUFACTURING TECHNOLOGY LABORATORY**

Aeronautical Systems Division  
United States Air Force  
Wright-Patterson Air Force Base, Ohio

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ABSTRACT - SUMMARY  
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ASD TECHNICAL REPORT 62-7-788  
August 1962

DEVELOPMENT OF MANUFACTURING METHODS FOR  
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J. J. Aclin  
et al  
Olin Mathieson Chemical Corporation

Prototype production processes have been demonstrated feasible for preparation of glass flake resin premixes and subsequent fabrication of parts by compression molding, transfer molding, calendering and centrifugal casting. Laminates have exhibited physical properties in most instances superior to reported characteristics of many glass reinforced premixed systems. Processing premixed systems by either compression molded preforms (dry blends) or calender orientation (wet blends) yields laminates having excellent appearance, free of voids, wrinkles, opalescent areas, disoriented areas, and other visible flaws. Preforms of dry blends can be compression molded into simple shapes which retain the properties of the preform; calender oriented sheets can be compression molded or centrifugally cast into more complex shapes with equal results. Investigations of variables to determine factors influencing physical properties resulted in major efforts in screening of commercially available resin systems, and detailed studies of flake size breakdown during processing.

Economic and reproducible methods for premix preparation were developed based on the use of an Abbe blender for wet mixes and a Patterson-Kelley V blender for dry materials. Other techniques investigated but less satisfactory were plenum chamber coating, solvent coating and centrifugal blending. Processing techniques of extrusion, rotational molding and two roll milling were demonstrated impractical for processing glass flake resin premixes.

Resin classes investigated included epoxies, polyesters, phenolics and silicones. Epoxy and polyester resins are readily mixed and processed to complex shapes. Strength and visual characteristics of the epoxy systems were superior to polyester laminates. Phenolic and silicone resins produced poor appearing or uncured moldings.

Seven complex shapes, including missile fins, ablative nose cones, Davy Crockett nose cones, practice windshields, exhaust nozzles, electronic gates and electronic circuit frames were molded successfully in production equipment from 50% and 70% glass-epoxy resin premixes, and 50% glass-polyester resin premixes.

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# FOREWORD

This Final Technical Engineering Report covers the work performed under Contract AF 33(600)-41885 from 8 October 1960 to 7 June 1962. The manuscript was released by the author 13 July 1962 for publication as an ASD Final Technical Engineering Report.

This contract with Olin Mathieson Chemical Corporation, New Haven, Connecticut, was initiated under Manufacturing Methods Project 7-788, "Development of Manufacturing Methods for Glass Flake Reinforced Plastics". It was accomplished under the technical direction of Mr. Dorsie C. Harleman of the Chemical Engineering Branch (ASRCTC), Manufacturing Technology Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

Mr. J. J. Aclin was the Project Engineer in charge of the program at Olin Mathieson. Others involved in the Research of the program are A. D. Snyder, L. J. Klahs, and F. E. Manemeit.

This project has been carried out as a part of the Air Force Manufacturing Methods Program. The primary objective of the Air Force Manufacturing Methods Program is to develop on a timely basis manufacturing processes, techniques, and equipment for use in economical production of USAF materials and components. The program encompasses the following technical areas:

Rolled Sheets, Forgings, Extrusions, Castings, Fiber and Powder Metallurgy Component Fabrication, Joining, Forming, Materials Removal Fuels, Lubricants, Ceramics, Graphites, Non-metallic Structural Materials Solid State Devices, Passive Devices, Thermionic Devices.

Your comments are solicited on the potential utilization of the information contained herein as applied to your present or future production programs. Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

\*\*\*\*\*

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

*Walter B. Hughes*  
WALTER B. HUGHES  
Lt. Colonel, USAF

Chief, Manufacturing Technology Laboratory  
Directorate of Materials and Processes

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## I. Introduction

Aircraft and space hardware requirements demand structural materials possessing high tensile strength, low density and a high flexural modulus. Further, a significant requirement is that these properties be nearly equal in all directions.

Glass flake reinforced laminates possess high flexural modulus which is approximately proportional to the glass content. The tensile strength to weight ratio of these laminates is equal to or higher than most other structural materials. These factors, together with the nature of glass flake-resin mixtures, led to the determination of the feasibility of processing mixtures and fabrication of complex shapes using automatic machinery, rather than hand fabrication, which is the general method for preparing glass cloth reinforced structural plastics.

Early studies of glass flake laminates indicated major difficulties in obtaining sound structural pieces would be encountered with incomplete wetting or coverage of glass flake by the resin, disorientation of the flake, and non-uniformity of distribution. Through carefully controlled experimentation, techniques were developed which overcame all of these shortcomings. A new variable, the non-uniformity of glass flake, and its degradation of particle size through processing appeared as the major contributing factor to high strength in laminates prepared using commercially available resins. While two processes having commercial potential were developed for fabrication of end items without additional flake degradation, the breakage experienced in preparing flake resin premixes controlled the ultimate strength of the laminate.

This study concerned itself with the relative value and usefulness of epoxy, polyester, phenolic and silicone resin classes as binders for glass flake. Most systems were evaluated at 50% and 70% glass contents. Processing techniques investigated included mixing by Abbe blending, dry (Patterson-Kelley) blending, plenum chamber spraying, solvent coating and two roll milling. Fabrication processes included compression, transfer and rotational molding, calendering, extrusion, injection molding and centrifugal casting.

## II. Conclusions

From the investigations, development effort and prototype production process demonstrations undertaken, it is concluded that:

### A. Resins:

1. Epoxy resins produce superior premixes and are capable of being fabricated into useful complex shapes by some conventional plastic processing techniques;
2. Polyester resins can be premixed equally as well as epoxy systems, however laminates in general have poor visual characteristics and lower strength.
3. Phenolic systems yield poor laminates as a result of excessive blistering.
4. Silicone resin cure cycles are difficult to control and too lengthy for economic processing.

### B. Mixing

1. Premixes may be prepared economically and with facile processing using either an Abbe blender for wet premixes or a Patterson-Kelley V blender for dry mixes.
2. Other mixing techniques are cumbersome, yield inadequate flake wet out, excessive flake breakdown, and are more costly to operate and maintain.
3. All mixing techniques investigated result in significant reduction in the size of the glass flake. This breakdown constitutes a major hindrance to obtaining high strength laminates using conventional resins and processing techniques.

### C. Fabrication Techniques

1. The roller calendering process for orienting flakes prior to molding permits consideration of the feasibility of glass flake laminates in a wide variety of end products including ablative heat shields as well as radomes, printed circuit boards, and other items requiring unusual dielectric properties.
2. Standard production processes of compression and transfer molding yield complex shapes from glass flake premixes without process difficulty. These articles have strengths superior to those fabricated from most commercially available premix materials.

3. A centrifugal casting process shows promise for a wide range of cylindrically shaped objects.
4. Roller calendering and centrifugal casting do not appear to cause additional glass flake degradation over that resulting from mixing.
5. Additional glass flake breakdown is experienced in compression and transfer molding of unoriented premixes.
6. A process for wetting out glass flake without degradation, combined with a part fabrication technique based on calendering or centrifugal casting, is expected to yield physical properties considerably higher than obtained in these studies.
7. Glass flake premixes do not perform satisfactorily in extrusion, injection molding, rotational molding or two-roll milling operations. Unuseable objects were produced during experimental studies.
8. Calender oriented sheet, either wet or B-staged, should be adaptable to vacuum bag and pressure bag molding as well as compression molding and centrifugal casting as demonstrated herein.

#### D. Physical Characteristics of Laminates

1. Using commercially available resins, strengths of laminates produced in this program did not meet the target specifications.
2. Low strengths were attributed exclusively to the breakdown in glass flake size resulting from processing.
3. New resins and processes which do not cause reduction of flake size are expected to yield laminates having higher strengths than target specifications.

### III. Phase I - Literature Survey

#### III.1. Summary of Prior Art

A comprehensive survey of the literature relative to the use of glass flake in the fabrication of reinforced plastic laminates was made prior to initiating laboratory and pilot plant studies. The use of flake-glass reinforced laminates has the potential of high modulus, uniform strength in all directions, low moisture permeability and higher glass loadings than the common fiber glass and glass cloth reinforced laminates. Tensile strengths, however, are much poorer than in fiber glass and glass cloth laminates. They range to a maximum of 29,000 psi. (7)

Of the various resin systems investigated, epoxy resin binders were reported to be the most satisfactory, i.e., to have the highest strength properties. Phenolic, polyester and silicone resins were all comparatively inferior to the epoxy systems.

Further refinement in optimizing strength properties of flake reinforced laminates generally appeared to lie in the following approaches: (3), (8), (7), (6)

- a. Preparation of a laminate having a high glass flake content.
- b. Absence of absorbed or included air bubbles.
- c. Perfect parallelism of flakes within the laminate.
- d. Accomplishment of a constant and minimum resin binder thickness (less than 60 microns) combined with a complete wetting of flakes by the resin. (At high binder thicknesses, resin failures alone have been noted. Decreasing this thickness allows increased contribution of stress acceptance by the flake glass which possess very high tensile strength.)
- e. Use of a glass flake of predetermined size or diameter to thickness ratio (generally agreed to be 400-1000).
- f. Use of low shrinkage resins.

#### III.2. Background

A continued interest within the military for reinforced plastic structural materials, led to the investigation of flake glass as a reinforcing material principally because a higher strength to weight ratio is conceivably possible. In addition, a glass flake in a composite can theoretically provide a multi-directional stress acceptance as opposed to a glass fiber or a glass fabric composite having only uni- and bi-directional strengths respectively. (3)

A higher modulus of elasticity, due to fewer degrees of freedom, could also be expected from a glass flake reinforced laminate. Furthermore, size considerations allow a higher loading, or weight of glass flake per unit volume of laminate, which theoretically could result in higher strength properties of the laminate.

Tests have shown that the flake glass laminates are extremely good barriers for preventing diffusion of water and solvent vapor (almost as effective as aluminum foil). (6)

Considering mentioned properties, applicability of this material is extensive. Suggested military applications are:

- a. Rocket exhaust nozzles.
- b. Rocket cases.
- c. Rocket fins.
- d. Aircraft and missile radomes.
- e. Moisture barrier and corrosion-resistant coatings.

### III.3. Synopsis

#### III.3.1. Flake Manufacture (1)(2)(3)

Methods for fabrication of flake glass have evolved from Emhart, Armour Research Foundation, Linden Laboratories, and Owens-Corning Fiberglass Corporation. The methods developed by Emhart consist of stretching molten glass into a film having inclined axes; rolling glass beads, glass tape; blowing extruded ribbons of glass, and drawing tape from a lip. Narmco used techniques of feeding fiber glass into a flame to develop molten beads and subsequently rolling them into thin discs. Armour experimented with blowing bubbles from molten tubing; flame spraying frit; and "enameling" glass on various surfaces. Linden's procedure consisted of blowing glass tubing. The method adopted by Owens-Corning was the blowing of bubbles in molten tubing and crushing the bubbles into flakes. This method was predominantly successful although it produced a variety of flake shapes. These flakes had varying diameters, irregular notched edges, and a slight curvature since they were formed from a curved surface.

The strength of formed glass flakes and glass ribbons varies inversely with the thickness. Individual glass ribbons of two-micron thickness have yielded a tensile strength of over 200,000 psi. (2)(3)(7)(8)

#### III.3.2. Resin Premix - Process Techniques (1)(3)(6)(7)

Mixing and wetting the glass flake with the desired resin binder is the major problem in the fabrication of laminates. This has been accomplished by:

1. Hand kneading in a polyethylene bag.



2. Mixing in an electric "kitchen" type mixer (some reduction of flake size).
3. Spraying aerated flakes in a chamber followed by molding, or B-staging followed by molding.
4. Dry blending powdered, catalyzed and uncatalyzed resins followed by molding.
5. Compounding a premix on a differential two-roll mill (reduction of flake size).
6. Mixing the composite in a Baker-Perkins mixer (appreciable reduction of flake size).
7. Centrifugal resin and glass flake to form a composite.

Methods 1, and 3-7, inclusive, had been performed by Olin Mathieson in work pursued prior to the award of the subject contract.

~~Problems that have been recurrent with most fabricators of laminates have been:~~

1. Air bubbles in laminates.
2. Insufficient coverage of glass flake with resin.
3. Non-parallelism or misorientation of individual glass flakes in the laminate.
4. Variation of resin binder thickness.
5. Accurate control of glass content in final laminate.

### III.3.3. Laminate Properties

Strength properties of laminates have been reported to be favorably affected by a flake having a high ratio of diameter to thickness. Laminates prepared from classified mixtures of glass flake (-10 mesh +50 mesh) have shown higher tensile strength. Some data are anomalous, as those in a report of work performed at Narmco (October 1960, Quarterly Report #2, Contract AF 33(616)-7195) which showed that tensile strength of flake reinforced laminates composed of flakes with average diameters of 200-4,000 microns had no relationship to flake size.

Ideally, a flake having a perfectly uniform diameter and thickness with completely parallel edges, and no included strain or surface flaws, would be desired for use; however, no such material has been produced. Surface treatments to anneal flaws or to etch flakes have resulted in poor laminates. Heat-treated glass shows

some evidence of improving laminate strengths although more work is required to prove this system. Surface treatments of glass flake with bonding agents have not materially affected the properties of laminate made with epoxy resins. Data on surface treatments of glass flake with bonding agents for use with other resin systems (polyester, silicone, phenolic) are limited and generally appear to indicate a deleterious effect on laminate strength.

Epoxy resin binders combined with polamide gave the best strength characteristics of flake-reinforced composites. The strong polar adhesion of epoxy resin functional groups to the hydroxyl groups of the glass flake is obviously important in this well known wetting action of epoxy resins with glass. Epoxy resins, when warmed, gave low viscosity materials which had the best wetting characteristics. Strengths obtainable with epoxy-type resin binders were: (7)

1. 26,000 psi max. tensile strength
2. 54,000 psi max. compressive strength
3. 47,000 psi max. flexural strength

Polyester resin binder systems, (6), (1), (7) were all inferior to epoxy systems.

Phenolic and silicone resin binders had an added disadvantage, namely that of formation of volatile material during curing. (1)(7)

Diallylphthalate resin binders used did not cure sufficiently. (6)

#### III.4. Conclusions

The glass flake reinforced laminate has exhibited higher modulus properties than common reinforced laminates. The tensile strength of the prepared samples are relatively poor (a maximum of 29,000 psi). Most of the work has been performed with epoxy resin binder systems.

The potential of this novel reinforcement cannot be fully realized or evaluated because of major mechanical processing limitations in the present state of the Art. Crude blending techniques used to coat glass flake with resin have all exhibited serious shortcomings which have resulted in major decreases in laminate physicals. Molding parameters were relatively unknown and all empirical in nature.

The laminates tested have generally been of poor quality and therefore data obtained has been considered to be a value which can be surpassed. Almost all tensile specimens have exhibited a tendency to fail at a fault or imperfection in the laminate.

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#### IV. Phase II Investigation of Production Methods

##### IV.1. Background

In establishing the techno-economic feasibility of production methods for glass flake reinforced laminates, Phase II of the contract was devoted to experimental and pilot plant studies of mixing and fabrication techniques. These investigations were carried on throughout the contract period, concurrent with and in succession to Phase III, "Fabrication of Selected Samples." Major problems concerned with visual appearance of early specimens, and low strengths of laminates, led to extensive investigations of variables and corrective actions.

Discussion pertinent to work performed in Phase II has been divided into five subsections as follows:

1. Cast Resin Systems
2. Blending Techniques
3. Premix Processing
4. Molding Techniques
5. Characteristics of Processed Glass Flake

##### IV.2. Summary of Experimentation

###### Cast Resin Systems

Investigations of unreinforced resin systems were made to select candidates offering the greatest potential compatibility with glass flake in fabrication of high strength laminates. A total of 51 epoxy systems, 11 polyester systems, 15 phenolic, and 9 silicone resins were screened. In these studies the obvious superiority of epoxy systems was noted which led to the use of this resin type for process screening studies.

###### Blending Techniques

Methods studied in efforts to produce high quality glass flake resin mixtures included Abbe mixing, dry blending, plenum chamber and solvent coating, two-mill coating and centrifugal mixing. After exhaustive studies, Abbe mixing was selected as a reproducible process for making wet resin blends, and a Patterson-Kelley V blender was determined to be adequate for dry resin mixtures containing glass flake.

###### Premix Processing

Early experimentation demonstrated the need for development of premolding processing to eliminate flaws in laminates resulting from molding bulk premixes. Dielectric heating, extrusion, injection molding, compression molding and calendering were investigated as methods for preform preparation. The most successful technique

developed was based on the calendering operation in which glass flake was oriented without degradation of particle size. Premixes could be processed into either wet or B-staged sheets throughout this process.

#### Molding Techniques

Detailed pilot studies of molding processes included investigations and evaluations of compression and rotational molding as well as centrifugal casting. Experience with compression molding led to the decision to study molding in production equipment. While both compression and transfer molding proved adaptable with bulk premixes, superior laminates were obtained from calendered sheets processed by compression molding and centrifugal casting.

#### Characteristics of Processed Glass Flake

Evaluation of laminate properties indicated variables other than orientation of flake and resin thickness to be limiting. A comprehensive investigation of glass flake particle size reduction demonstrated a controlling influence on ultimate laminate strength. Fabrication techniques (calendering and centrifugal casting) were developed which contributed negligible breakdown; however, the process of Abbe mixing flake and resin produced severe degradation.

### IV.3. Experimental Detail

#### IV.3.1. Cast Resin Systems

Resin systems from epoxy, polyester, silicone and phenolic classes were screened with emphasis being placed on systems having inherent high strength. The epoxy resins having shown the most promise in the past for high strength glass laminates, were selected for most initial process studies. The hardener systems were chosen with the blending technique and the final fabricating mode in mind. Viscosity, pot life, and the exothermic nature of the curing cycle were also considerations.

In all cases, choice of resin systems and formulations were restricted to solventless systems because of known impermeability of the glass flake in the final laminate, which causes extreme difficulty in removal of mechanically bound solvent molecules during curing cycles.

A summary of cast resin systems that were tested is presented in Table 1.

The curing agents considered have been of several types:

- a. Catalytic (i.e. promoting self-polymerization of the resin).

b. Polyfunctional curing agents (active hydrogen of curing agent reacts or adds to epoxide ring of resin).

1. Aliphatic polyamines
2. Modified aliphatic polyamines
3. Aromatic polyamines
4. Anhydrides and polyfunctional acids

The boron-trifluoride monoethylamine ( $\text{BF}_3\text{-MEA}$ ) complex was chosen because it imparted long pot life to the resin used. Difficulty was experienced in the curing of the  $\text{BF}_3\text{-MEA}$  systems. Other catalytic curing agents gave too short a pot life at room temperature. Type b1 agents were neglected for the same reason. Type b2, modified aliphatic polyamines, also have short gel time. However, a commercially available polyamide, Versamid 115, was evaluated and showed interesting elastic properties. m-Phenylene diamine, type b3, has been used extensively because it imparts good physical properties. Additionally, it formed B-stage resins with good stabilities. Hexahydrophthalic anhydride, type b4, offers an excellent pot life and retention of physical properties at elevated temperatures, as do most of the anhydrides and polyfunctional acids.

Epoxy resins chosen vary in chemical structure, molecular weight and epoxide equivalent weight from the di-glycidyl ether of bis-phenol to di-epoxide structure.

Testing on cast epoxy resins and all others presented here has been in accordance with current ASTM Standards.

The formulation studies conducted were used as an aid in screening out resins having too low a tensile strength and brittleness combined with poor wetting factors as evidenced by high viscosity, and high surface tension.

Peroxide catalysts were predominantly used for polyester systems. Benzoyl peroxide was used because of its long pot life at room temperature. Other catalysts such as methyl ethyl ketone peroxide, ditertiary butyl peroxide, (low temperature catalysts) were also evaluated. Polyester resins chosen are standard styrene-modified, unsaturated resins, (i.e. the polyester produced from reaction of maleic anhydride and diethylene glycol).

Dicumyl peroxide is an acceptable curing agent for the chosen silicone systems. The Dow-Corning resins chosen were the recently developed solventless resins.

Hexamethylene tetramine is used as a standard catalyst with phenolic formulations. However, very few phenolics are prepared commercially as solventless systems. One such solventless system was obtained from Union Carbide Chemicals Company. Strong exothermic curing and overcuring were observed combined with a short pot life.

#### IV.3.1.1. Discussion of Resin Testing

Table 1 presents the physical properties of resin systems which were tested. The resins were prepared with the desired hardener system in accordance with the resin or catalyst manufacturers' recommendations. In most cases, the uncatalyzed resin was degassed at a vacuum of 0.2-1.0 mm. Hg. unless the resin had an appreciable vapor pressure and would lose monomeric material under reduced pressure. This technique of degassing resulted in relatively bubble-free castings.

The mixed catalyzed resin was then cast into sheets 10" x 10" x 0.135-0.160" thick and 7/8" x 7/8" x 6" bars which were later machined to 1/2" x 1/2" x 5" bars for heat distortion bars and 1/2" x 1/2" x 2-1/2" notched bars for impact testing. All systems were gelled at room temperature or slightly above when using a high temperature catalyst. Thereafter, bars and sheets were subjected to time and temperature heat-curing and post-curing cycles.

During the program, it was discovered that thicker bars cured at different rates and the exothermic reaction in the thick bars caused crazing and cracking of the bars, making them unsuitable for testing. Since considerable time would have been expended in reformulating resin batches and determining separate cure cycles for the thick bars, many of the resin systems were not re-examined in the thicker dimensions. Tensile strength served as an effective indication of proper cure accomplishment.

Tensile strength data reported are in general agreement with manufacturers' specifications. Tensile value for some of the systems were not supplied by resin manufacturers. A spread in tensile values obtained is due in part to sample preparation technique. For example, in early samples micro-nicks were formed in many samples when the double-fluted "Tensilbit" was used to shape tensile specimens. Changing to a diamond plated "Tensilbit" has almost entirely eliminated the problem.

#### IV.3.1.2. Test Procedures

Test procedures used to evaluate cast resin systems were ASTM method.

##### 1. Tensile Strength - ASTM D638-58T

Tensilbars were prepared by band sawing resin strips from cast sheet followed by milling in a Tensilbit Machine equipped with a No. 51-702T double-fluted carbide tipped Tensilbit.

This Tensilbit was later replaced with a 51-700D diamond plated Tensilbit, which prepared essentially nick-free specimens.

TABLE 1

Physical Properties of Cast Epoxy, Polyimides, Siloxanes, Phenolic Resins

Identification	Formulation	Composition	Sample Weight	Tensile Str. $\times 10^3$		Tensile Modulus $\times 10^4$ psi	Heat Distortion Temp. $^{\circ}\text{C}$	Load Deflection Rate	Impact (notched) ft.-lb./in. notch	Decomposition Temp. $^{\circ}\text{C}$	Remarks		
				ASTM D 638	ASTM D 638								
E-1-140201	EPB	16 PBR	7	6.49	3.37-3.34	4.99	4.57-5.10	241	139-142	72	58-92	D90	Deposited R.T. Difficult to stir. 100-150 added as solid
E-2-1-140202	EPB	16 PBR	8	7.44	4.93-12.25	4.49	5.43-5.53	121	118-124	46	41-81	D90	Deposited R.T. Difficult to stir.
E-3-140203	EPB	16 PBR	7	9.92	5.27-12.15	4.44	4.04-4.96	124	121-128	46	46-95	D90	Deposited 150 $^{\circ}\text{F}$ . Deposited quite readily.
E-4-140204	EPB	50 PBR	7	7.54	7.14-7.48	3.15	2.67-3.90	50	64-53	37	37-42	D97	Deposited 150 $^{\circ}\text{F}$ . Gel time about 10 min. at this temp. Impossibility to deposit at lower temp. because of high viscosity
E-5-140211	EPB	3 PBR	6	5.34	4.70-4.13	0.58	8.93-9.05	-	-	-	-	D90	Deposited 150 $^{\circ}\text{F}$ ; large smooth cracked bars
E-6-140208	EPB	3 PBR	3	4.02	4.00-4.04	4.33	2.62-4.38	-	-	-	-	D90	Bars not cast. Poor compatibility between resin and EPB.
E-7-140209	EPB	3 PBR	-	-	-	-	-	-	-	-	-	-	Sheet and bars as good for testing purposes. Swelled and bubbled. Buckle in casting.
E-8-140212	EPB	16 PBR	6	9.79	5.25-11.12	4.16	3.16-4.89	126	134-127	73	42-79	-	Deposited 150 $^{\circ}\text{F}$ . Comparable to MD-3
E-9-140215	EPB	15.4 PBR	6	11.33	4.55-13.68	4.57	4.25-5.14	99	-	-	-	-	No appreciable loss of viscosity when 528 and 216 added
E-10-140216	EPB	15.4 PBR	6	11.02	10.42-11.43	3.69	3.28-3.70	-	-	-	-	D96	Deposited at 150 $^{\circ}\text{F}$
E-11-140221	EPB	0.02 PBR	-	-	-	-	-	-	-	-	-	-	Ch. at 150 $^{\circ}\text{F}$ blended with equal amount of 504 and added to same portion parts R.T.
E-12-140222	EPB	16 PBR	-	-	-	-	-	-	-	-	-	-	Bars deposited at 150 $^{\circ}\text{F}$ and solid EPB added melted and solution deposited 150 $^{\circ}\text{F}$ ; sheet extremely hard to peel from glass plate and discarded.
E-13-140223	EPB	50 PBR	-	-	-	-	-	-	-	-	-	-	Bars as above with the exception that MMA initiator added did not help gel time, again necessary to discard sheet because it stuck to the glass plate
E-14-140225	EPB	52 PBR	6	2.99	2.12-3.36	-	-	-	-	-	-	-	Excess material only.
E-15-140226	EPB	52 PBR	-	-	-	-	-	-	-	-	-	-	For dry blending.
E-16-140227	EPB	50 PBR	-	-	-	-	-	-	-	-	-	-	Extremely difficult to gel. Finally gelled after 27-1/2 hrs. at 150 $^{\circ}\text{F}$ ; cracked glass and sheet; discarded
E-17-140228	EPB	1-2-4 HX	-	-	-	-	-	-	-	-	-	-	Called slowly 3 hrs. 120 $^{\circ}\text{F}$ ; cured 4 hrs. 250 $^{\circ}\text{F}$ .
E-18-140229	EPB	1-2-4 HX	7	4.55	2.86-5.17	-	-	-	-	-	-	-	Called slowly 4 hrs. at 250 $^{\circ}\text{F}$ .
E-19-140235	EPB	50 PBR	-	-	-	-	-	-	-	-	-	-	Called slowly 3 hrs. 180 $^{\circ}\text{F}$ ; cured 4 hrs. 250 $^{\circ}\text{F}$ .
E-20-140236	EPB	6.5 PBR	4	10.4	9.64-11.43	-	-	-	-	-	-	-	Very low viscosity liquid after mixing at 150 $^{\circ}\text{F}$ ; gel time about 20 hrs. 180 $^{\circ}\text{F}$ ; resin very brittle after cure cycle and unstable.
E-21-140237	EPB	90 PBR	-	-	-	-	-	-	-	-	-	-	Deposited at R.T. boils at lower pressure.
E-22-140238	EPB	13 PBR	-	-	-	-	-	-	-	-	-	-	Was not necessary to deposit: viscosity quite low necessary to gel at 150 $^{\circ}\text{F}$
E-23-140239	EPB	15	6	6.73	3.20-5.57	5.86	4.97-6.94	-	-	-	-	-	Very difficult to work with a heterospecific mixture very difficult to gel; crystallized and discarded
E-24-140240	EPB	15	6	5.36	3.59-7.33	4.13	3.23-4.64	-	-	-	-	-	Gel time 12 hrs. 180 $^{\circ}\text{F}$ ; cure cycle not complete
E-25-140241	EPB	25 PBR	-	-	-	-	-	-	-	-	-	-	Sample not prepared at this time
E-26-140242	EPB	15	-	-	-	-	-	-	-	-	-	-	Gel time 23 hrs. 180 $^{\circ}\text{F}$ ; cure cycle not complete
E-27-140243	EPB	15	-	-	-	-	-	-	-	-	-	-	Sample not prepared at this time



Key to Table 1FormulationsEpoxide and Di-epoxide Resins

ES28 - Epon 828 - Shell Chemical Company  
JD510 - Epi Rez 510 - Jones Dabney Company  
JD504 - Epi Rez 504 - Jones Dabney Company  
U201 - Unox 201  
U206 - Unox 2206 - Union Carbide Chemicals Co. (diepoxides)  
U207 - Unox 207

Polyesters

L4128 - Laminac 4128 - American Cyanamid Company  
V156 - Naugatuck Chemical Company

Silicones

DC7145 - Dow-Corning Company  
DC7146 - Dow-Corning Company

Phenolic

C7541 - ERB 7541 - Union Carbide Plastics Co.

Curing Agents

MPD - Metaphenylenediamine - Allied Chemical Co.  
BF<sub>3</sub>-MEA - Boron Trifluoride Mono-ethylamine Complex -  
Harshaw Chemical  
V115 - Versamid 115 Polyamide Resin - General Mills Co.  
HHPA - Hexahydrophthalic Anhydride - National Aniline Div. -  
Allied Chemical  
AMEA - Alpha Methyl Benzyl Amine - Union Carbide Chemicals Co.  
1,2,6, Hex- 1,2,6 Hexanetriol - Union Carbide Chemicals Co.  
DMP-10 - Accelerator - Rohm and Haas Co.  
MA - Maleic Anhydride - American Cyanamid Co.  
TMP - Trimethylol Propane - Heden Newport Chemical Co.  
BENZ. P - Benzoyl Peroxide - Harshaw Chemical Co.  
HEXA - Hexamethylene Tetramine - Matheson, Coleman and Bell Co.  
DICUP - Recrystallized Dicumyl Peroxide - Hercules Powder Co.  
LP-3 - LP-3-polysulfide resin (Flexibilizer) - Thiokol Chemical Co.

Tensile strength determined on a Tinius Olsen Plastiversal Machine - separable (S-2) and nonseparable (U-2) strain indicators used.

## 2. Tensile Modulus

Calculated by obtaining the slope of the load vs. elongation curve and multiplying by the ratio of gage length to cross-sectional area. In cases where the nonseparable extensometer was used, all modulus calculations were made at 50% of ultimate elongation by approximating a line parallel to the curve at that point and passing through the origin (0 load, 0 elongation). In some cases, a separable extensometer (S-2 strain instrument) was used for recording load elongation data of the cast resins. In those cases, a line passing through the origin tangent to the curve was used in calculating modulus values.

## 3. Heat Distortion Temperature

### ASTM D648-56

Cast bars were machined to the required  $1/2" \times 1/2" \times 5"$  dimensions. Tests were run in accordance with ASTM specifications.

## 4. Izod Impact (Notched)

### ASTM Test D256-56

Cast bars were machined and notched in accordance with ASTM recommendations. Impact tests were conducted on a Tinius Olsen Change-O-Matic Impact Tester.

## IV.3.1.3. Conclusions

The information on cure and resin handling characteristics which was obtained during this phase of the program was used throughout the program. Without prior knowledge of viscosity, process ability and pot life of particular resin blends, the completion of the program would have been difficult. In addition, comparison of physical properties and determination of effectiveness of flake reinforcement would have been impossible.

Based upon data obtained in this study, several representative resin-cure systems were chosen for each of the four resin types under consideration.

The Jones Dabney 510-MPD system was used as the basis of most of the epoxy resin systems in preference to the Epon 828 or Unox resin systems. Epon 828 was not used because of dermatitis reactions experienced by contract personnel. Unox 207, Unox 201-HHP, DMP-10 systems were used where long pot life was a requirement.

The polyester resin system chosen because of optimum handling conditions was Laminac 7128-decarp (dicumyl peroxide) an improved version of Laminac 4128.

A solid phenolic resin RI 4009 was used for dry blending after the flake laminates prepared with the liquid C-7541 were proved to be of poor quality. The dry, pulverized RI 4009 was not evaluated as a solution casting resin.

The Dow-Corning silicone resin series were evaluated only in massed glass flake systems because of the extreme difficulty encountered in preparing acceptable oriented glass flake laminates. Silicone resins produced the poorest laminates because of curing problems and a tendency to stick to the polished mold surface regardless of the parting agent used on the mold.

#### IV.3.2. Blending Techniques

The first step in the preparation of glass flake laminates was to develop a method of combining the glass flakes with the selected resin system. The wide range of plastic binder systems which cover water-thin liquids through pastes and solids necessitated the development of more than one premix technique. Obviously, a blending method suitable for a water-thin liquid such as the plenum chamber method would be impossible for a solid resin system.

This section of the report is devoted to a discussion of the individual mixing methods evaluated.

##### IV.3.2.1. Abbe Mixers

The Abbe mixer is constructed as a mass and paste mixer, having a double "U" bowl construction and two modified sigma mixing blades rotating at a speed differential of 2 to 1 (maximum 50 rpm and 100 rpm). Blade construction is such that shear forces developed during mixing are substantially smaller than shear forces present in other mass and paste mixers. Prime applications for this mixer have been in the manufacture of premix glass fiber reinforced compounds, where minimum glass fiber degradation is a requisite.

#### IV.3.2.1.1. Abbe Mixer One-quart Size

The first glass flake premixes were prepared in a small, rented one-quart size Abbe mixer. Shorter mixing times, excellent wet-out of glass flake, and improved uniformity of mix at the 50% glass content over the other blending techniques were realized. Additional experiments proved that a wider variety of resin systems could be processed in the Abbe mixer. The early studies, using this equipment, were promising because of the improved mixing cycle resulting in an upgrading of the physical properties of laminates. Abbe mixing appeared to be the most economic mixing technique investigated, with the exception of the dry-blending technique.

In Table 2 a summary is presented of the laminates molded from the initial trial batches of premixes prepared with the small Abbe mixer. Classified flake glass in sizes of +8, -8 + 16, and -16 mesh were used as starting materials. Only epoxy-based resin formulations were evaluated in this preliminary study.

The epoxy-glass systems evaluated included polyamide (EL-20 Series) and polysulfide flexibilized (EL-21-1) cure systems. Polyamine curing agents such as meta-phenylene diamine were used (EL-5, 7, 19, 21) to promote enhanced properties. Anhydride hardeners were used when lengthened pot lives (EL-14, EL-18) were required.

At the low glass levels investigated, tensile strength properties ranged on the average from 6 to 17 thousand psi. The variations in tensile strength are attributable to void content and varying glass contents throughout the laminate. High void content implies a large number of dry spots or numerous air bubbles; conversely, low void content implies a desirable, low occluded air volume and a reduced amount of dry spots.

The void content of these Abbe mixed laminates was frequently high. A compression mold can be expected to reduce void contents as pressure can be applied to squeeze remaining air out of the sample in a confined cavity. Such a mold was not available at the time these studies were made.

Tensile and flexural properties of Abbe mixed materials are presented in Tables 2 and 3, respectively.

T A B L E 2

## PHYSICAL PROPERTIES OF LAMINATES PREPARED BY ARBE MIXING

Laminate Identification	Resin Formulation	Initial Content, g. Wt. %	Glass Mixing Size Method	Cure Cycle			Laminate Properties		Tensile Strength			Tensile Modulus	
				Step	Hrs.	Time Temp., °F.	Press., psi	Thickness, Inch	Density, Gr/cc	Glass %	Voids, %	x 10 <sup>-3</sup> psi	x 10 <sup>-6</sup> psi
EL-5-1	JD 510 MPD 14	55	+8M	1 2	1 3	200 300	C O	.125	-	-	-	6.37 6.50	-
EL-5-3	JD 510 MPD 14	51.1	-8M +16M	1 2	1 3	200 300	C O	.125	1.585 1.599	55.2 54.5	6.4 5.2	9.36 10.42	3.03 3.40
EL-7-1	JD 504 MPD 14.7	45	+8M	1 2	1 3	200 300	C O	.125	1.498 1.428	47.9 47.8	5.4 6.6	10.72 13.0	3.64 5.34
EL-14-2V	JD 510 HHPA 50 DMP-10 .5	50	+8M	1	3	300	C	.064	1.68	44 47	0	14.7 17.0	2.43 2.97
EL-14-2-3	JD 510 HHPA 50 DMP-10 .5	70	+8M	1	3	300	C	.226	1.81	66	-	9.15	-
EL-18-3V	JD 504 HHPA 50 DMP-10 .5	50	+9M	1	3	300	C	.106 .118	1.63	46	0	11.2 12.9	6.46
EL-19-1	JD 510 JD 504 25 MPD 14.9	50	-16M	1 2	1 3	200 300	C O	.125	1.395 1.492	59.9 56.5	20.3 12.5	6.24 7.60	- 2.62
EL-19-2	JD 510 JD 504 25 MPD 14.4	50	-8M +16M	1 2	1 3	200 300	C O	.076	1.453 1.503	51.7 51.3	11.8 8.4	12.3 14.6	1.8 2.92
EL-19-3	JD 510 JD 504 25 MPD 14.4	50	-8M +16M	1 2	1 3	200 300	C O	.086	1.524 1.513	66.1 55.3	9.9 10.6	6.13 7.54	4.30
EL-20-1	JD 510 C-288 30	52.1	-8M +16M	1 2	1 3	200 300	C O	.125	1.428 1.470	52.0 62.1	9.8 14.6	7.83 10.53	1.36 2.06
EL-20-2	JD 510 C-288 30	50	-8M +16M	1 2	1 3	200 300	C O	.105	1.734 1.671	57.4 67.4	- 8.8	10.4 14.8	5.30 11.90
EL-21-1	JD 510 MPD 18 LP 3 54	50	-8M +16M	1 2	1 3	200 300	C O	.125	1.577 1.654	53.5 53.6	8.3 3.8	7.41 8.30	2.68 5.00

TABLE 3

## FLEXURAL STRENGTHS FOR LAMINATES

Prepared by Abbe Mixing

Laminate Identification	<u>Flexural Strength</u> psi $\times 10^{-3}$		<u>Flexural Modulus</u> psi $\times 10^{-6}$	
	Average	Range	Average	Range
EL-5-1	12.9	9.80 - 16.0	2.06	1.85-2.27
EL-5-3	22.1	19.2 - 22.9	2.77	2.65-2.89
EL-7-1	18.6	17.5 - 19.7	2.53	2.51-2.54
EL-19-1	15.3	13.6 - 17.2	2.40	2.26-2.65
EL-19-2	11.5	10.2 - 12.8	2.84	2.64-3.18
EL-19-3	15.5	13.7 - 16.9	3.14	2.84-3.37
EL-20-1	14.1	10.8 - 17.5	2.26	2.05-2.48
EL-20-2	17.1	15.5 - 20.8	2.51	1.98-3.05
EL-21-1	16.3	15.0 - 17.7	2.14	2.13-2.16
EL-14-2V	27.3	26.1 - 28.1	3.44	2.78-3.96
EL-18-3V	21.3	-	2.24	-

Prior to the addition of glass flake, the hardener (liquid or solid) was added to the resin binder and mixed in the bowl of the Abbe until the catalyzed resin was homogeneous. (Steam heat may be applied to the jacket of the mixer to reduce the viscosity of the resin and thereby promote better "wet-out" of the glass flake.) Glass flake was added to the resin with the mixer blades rotating. Mixing times vary as a function of formulated glass content, i.e. higher glass contents require longer mixing times.

Mixing time is considered to be one of the most important variables in producing high quality composites. There was to be expected an optimum mixing time below which resin coating on the glass flakes would be insufficient, and a mixing time above which excess flake breakdown would contribute to lower tensile strengths. To determine the optimum mixing time, three identical batches were formulated with the same glass content (50%), glass size (+8 mesh) and resin hardener system EL-19 (Table 4). Mixing times, only, were varied at 1-1/2, 5, and 10 minutes. After each batch was mixed, a sample was taken to determine the glass flake distribution. All three batches were cured into sheets by identical curing procedures outlined in Table 4. Five to seven strips were then cut from the cured sheets and tested for tensile strength. Figure 1 is a plot of average tensile strength vs. mixing time. Plotted on the same graph is a cumulative analysis of glass flake retained on a 50 mesh screen as a function of mixing time. As indicated in Figure 1, the five-minute mixing time resulted in the highest tensile strength, 8,900 psi, for the 50% glass level investigated. The screen analysis plot indicates that as mixing time increases, finer flakes are formed, reducing the cumulative percent retained on the 50 mesh screen. At the optimum mixing time, 39.7% of the glass flake is retained on the 50 mesh screen. (50 mesh was chosen as a convenient basis; any screen size could have been used to illustrate the relationship.) The above conclusions have resulted from tests performed using an Abbe mixer having a capacity of one quart.

#### IV.3.2.1.2. Abbe Mixer - 5-gallon Size

The initial success obtained with the one-quart Abbe mixer indicated the potential usefulness of this method of glass flake blending. The small size of the one-quart mixer restricted the nature of the studies and programs which could be evaluated. A five-gallon Abbe mixer was purchased and was used throughout the remainder of the program. The major portion of all the laminates, and all the premixes from which the subcontracted complex shapes were molded were prepared in this mixer.

It was necessary to prepare a test mix in the five-gallon mixer to objectively compare the breakdown of glass flake premixes in the five-gallon Abbe mixer with the breakdown encountered when the one-quart Abbe mixer was used. An additional objective was to gain insight into the mechanisms and rates of breakdown during the mixing cycle. Because of the limited batch size of the one-quart mixer rented during the earlier portion of the program, this study could not be conducted.

T A B L E 4

DATA USED FOR DETERMINATION OF  
OPTIMUM MIXING TIME IN ARBE MIXER  
FOR 50% GLASS FLAKE CONTENT

Laminate Identification	Mix Time Minutes	Tensile Strength		Per Cent Glass on Indicated Screen				Cumulative Wt. % on 50 M
		Average	Range	8	16	30	50	
EL-19-3	1 1/2	6.13	5.32-7.54	0	1.4	-	62.4	63.8
EL-19-5	5	8.90	5.70-15.7	0	0	4.6	35.1	39.7
EL-19-6	10	4.52	3.18-6.12	0	0	3.3	21.2	24.5

## Resin Formulations:

Jones Dabney Epi-Rez 510 99.9 g  
 Jones Dabney Epi-Rez 504 33.3 g  
 Metaphenylene Diamine 19.2 g

## Glass Content:

50%  $\pm$  0.5% at Start

## Glass Size:

+8 Mesh, 2 Micron Glass Flake

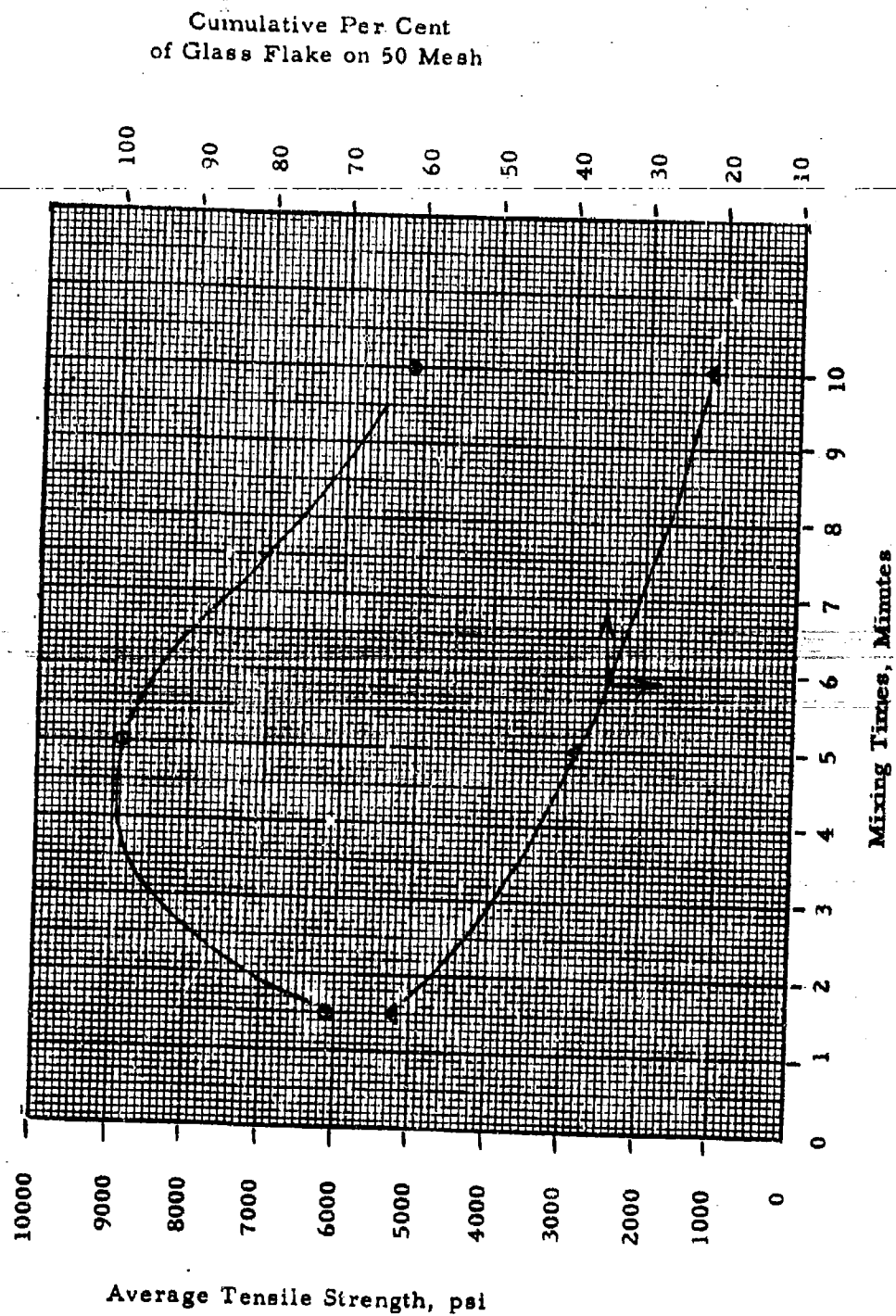
## Cure:

9 x 9 Laminate

1 hr. 200° F. Contact Pressure  
 3 hr. 300° F. Oven.



Figure 1  
Average Tensile Strength and Cumulative Per Cent Glass on 50 Mesh  
Vs.  
Mixing Time in Abbe Mixer



For the study, 8.8 pounds of unclassified glass flake were charged into the mixer and mixed with 8.8 pounds of Laminac 4128 (American Cyanamid) polyester resin catalyzed with one per cent benzoyl peroxide. During the mixing cycle, no heat was applied to the steam jacket of the Abbe mixer because of the sensitivity of the resin system to curing under slightly elevated temperatures. Mixing took place under 20 mm. Hg. vacuum for a total of 60 minutes. At 10-minute intervals, a 200-gram sample was removed from the batch and analyzed for glass flake size distribution.

The results of this study were:

1. The five-gallon Abbe mixer degrades the glass flake during mixing slightly more than the one-quart Abbe mixer.
2. During the mixing process, there is a very rapid disappearance of +8 mesh and +16 mesh flake. Similar to other mixing and grinding processes, there is a selective attrition of the largest flakes in the mix.
3. The percentage of flakes retained on the +100 mesh rises during the cycle, as expected (Table 5).

Figure 2 supports statement 1 above. The uppermost curve in Figure 2 represents the size distribution of unmixed, unclassified glass flake. The next curve progressing downward represents the distribution of glass flake size in a premix prepared in the one-quart Abbe mixer (Laminate EL-23-2). The lowest curve represents the analysis of the premix prepared in the five-gallon mixer after one-half hour of mixing, 1320 revolutions. (Earlier samples: 15 minutes, 25 minutes, showed insufficient flake wet-out as evidenced by poor compression molding containing dry glass flake.)

Both curves show a very similar distribution of size. Comparing the curves at the +30 mesh region, the horizontal separation between the curves shows that the five-gallon Abbe has degraded this flake size more than the one-quart Abbe mixer.

Figure 3 shows the amount of degradation that occurs during mixing. Both the +8 mesh and the +16 mesh glass flakes undergo rapid breakage in a short time. The +30 mesh fraction rises during the first ten minutes as the coarser +8 and +16 mesh flakes break down. Thereafter, the +30 mesh flakes are subjected to rather rapid size losses. Note that the abscissa of the graph is related to both mixing time and number of revolutions of the fast mixer blade. (Relating breakdown to revolutions in the mixer eliminates the required parameter of blade rpm.)

A much more comprehensive study of the effect of glass flake degradation due to processing and its relationship to laminate physical properties was performed at a later date and is reported in detail on another section of this report.

Table 5

Mixing  
Time  
in Abbe  
Mixer  
Minutes

Individual Weight Percent of Glass Flakes Retained on Indicated Mesh Size

	+8	-8+16	-16+30	-30+50	-50+100	Pan
0	52.5	43.5	14.0	7.0	3.0	Trace
10	trace	6.4	31.5	32.5	18.9	10.5
20	0	1.81	14.9	41.1	27.5	14.4
30	0	0.89	9.5	42.1	29.5	18.1
40	0	.07	5.2	33.1	34.7	26.9
50	0	trace	3.1	9.4	35.4	33.1
60 *	0	trace				

\*an error made during the analysis resulted in discarding the 60 minute sample

Figure 2

Comparative Glass Flake Distributions for Unmixed Unclassified Flake, Premixes from 1 Quart and 5 Gallon Abbe Mixer

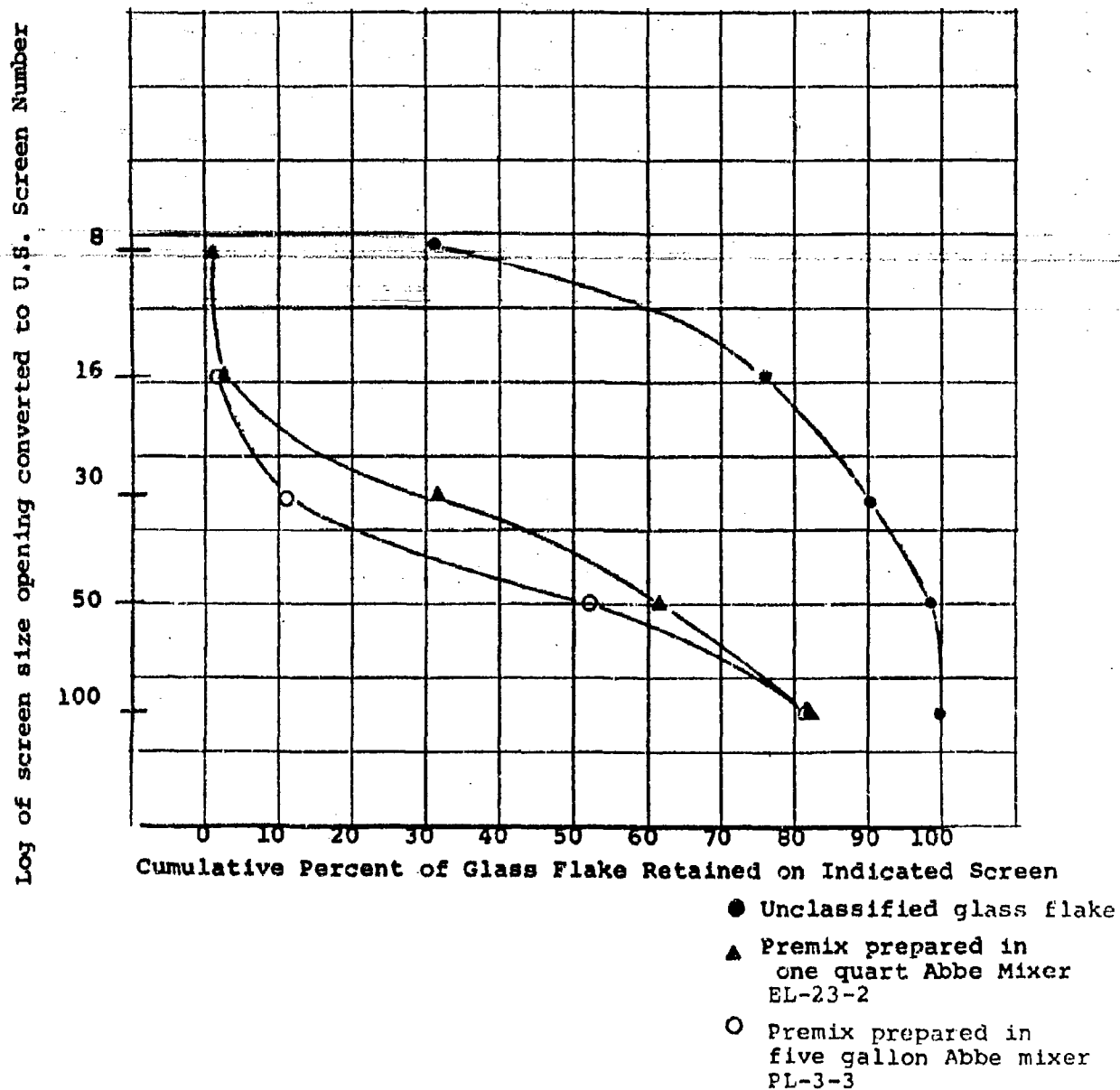
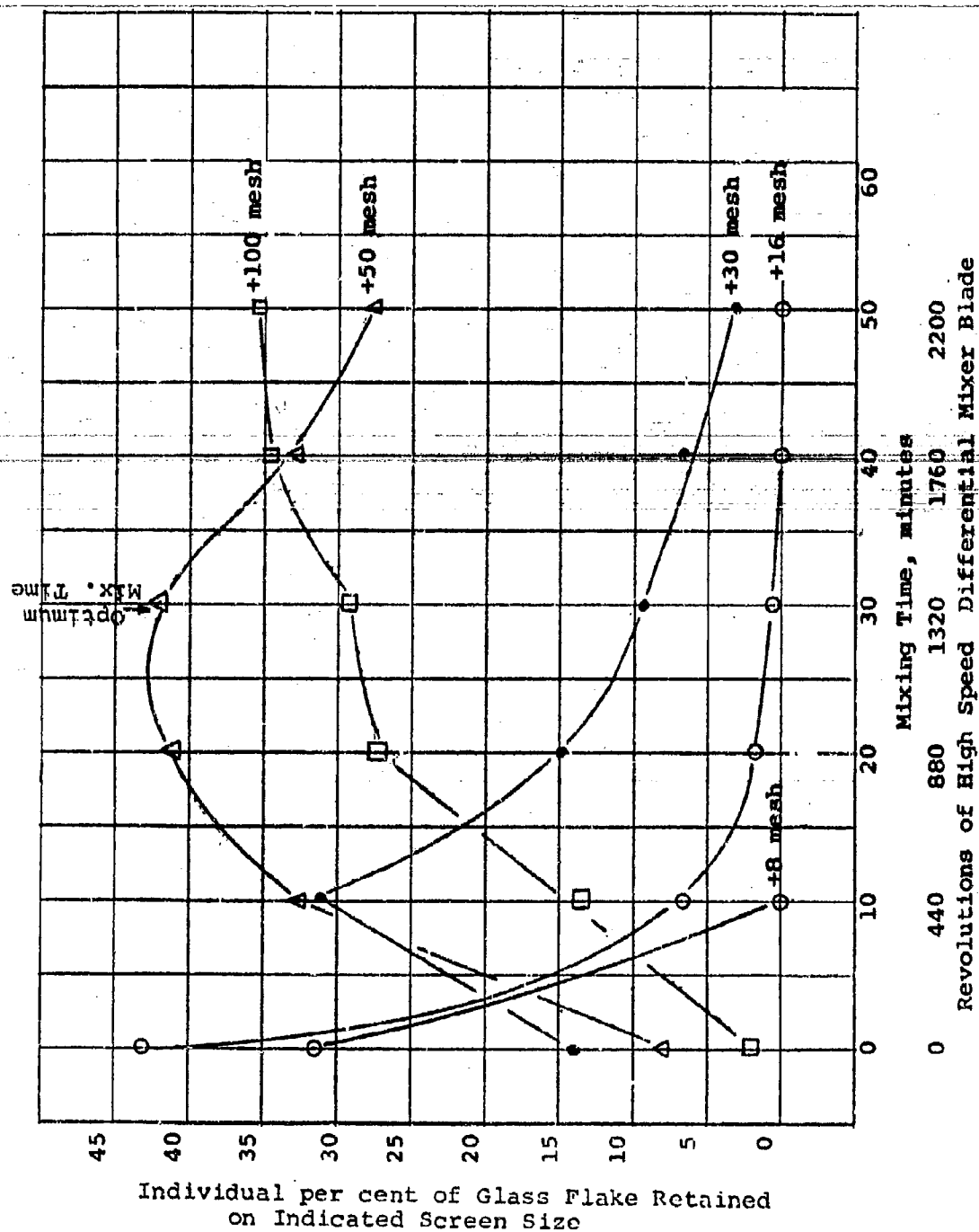


Figure 3  
Individual Screen Analyses of Glass Flake Size as a Function of  
Mixing Time in Five Gallon Abbe Mixer



#### IV.3.2.1.3. Abbe Vacuum Blending - 5-Gallon Size

The use of a vacuum blending technique for preparation of highly filled premix compounds generally results in increased mixing efficiency, i.e. the mixing time is decreased and filler wet-out is increased. We believed that similar benefits could be realized if a vacuum blending technique were perfected for the Abbe blending of glass flake premixes. We expected to decrease glass flake degradation through the reduction of mixing time.

The blend described in Table 6 was prepared using a vacuum blending technique. The resin and curing agent were blended together by hand and poured into the Abbe mixer. The Abbe mixing chamber was filled to the lip with loose, dry glass flake and the chamber was put under vacuum. When the pressure had dropped to below 10 mm. Hg., the mixer was started and was continued for about 3-4 minutes until all the glass had been wet out. The vacuum was broken and the Abbe chamber opened. The chamber was refilled and the cycle repeated. The preparation of this batch required the addition of the 3,000 grams of glass flake in four cycles. A total of 17 minutes was required to wet out the mass. Atmospheric blending of a batch of this size and glass flake content requires 30 minutes. Therefore a reduction of 33% in mixing time was realized. Unfortunately the addition of large volumes of dry flake en masse resulted in audible grinding noises being emitted from the mixer. The analysis of the glass flake breakdown resulting from this processing indicates a slight increase in breakdown of flakes did occur. A mechanical modification was made to the Abbe to permit slow addition of glass flake to the mixing chamber while under a vacuum.

The blend described in Table 7 was prepared using classified #8 mesh glass in a 60/40 flake to resin ratio. The hopper apparatus shown in Sketch 1 was used to add the flake gradually to the mixer. Difficulties were experienced because of a tendency of the glass flake to bridge over the opening and stop the flow of glass flakes into the mixing chamber. The resin system was weighed and added to the Abbe mixer and blended for 15 minutes under a full vacuum (1.0 mm. Hg.). The vacuum was broken, the mixer opened, and the glass flake added to the hopper chamber which had been installed on the apparatus (shown in Sketch 1). The hopper-mixing chamber seal was open while the vacuum was reapplied. When full vacuum was attained, it was found that the glass flake in the throat of the hopper chamber had bridged across the opening, preventing the flow of dry flakes from the hopper into the mixing chamber.

The vacuum was broken and the hopper reopened. The glass flake bridge was broken, the hopper lid replaced, the hopper-mixing chamber seal closed and the vacuum reapplied. When a full vacuum was attained, the hopper-mixing chamber seal was opened. Because of the pressure differential, the glass flakes flowed from the hopper into the mixing chamber. The flow continued for several minutes before the flakes once again bridged over the opening.

Table 6

	Glass Flake Breakdown Study						
	Abbe Vacuum Blend						
	<u>% +8</u>	<u>% +16</u>	<u>% +30</u>	<u>% +50</u>	<u>% +100</u>	<u>% Pan</u>	<u>% Loss</u>
Original Glass	73.6	11.5	5.1	6.0	2.9	2.0	2.0
Wet Premix	-	0.1	0.5	14.5	35.4	47.6	1.9
Wet Premix from Abbe Side Walls	-	-	0.5	9.7	33.9	54.2	1.7
Premix from Ram Extruder	-	-	0.5	12.4	36.7	48.0	2.4
Orientated 1st Pass	-	-	0.4	10.2	34.4	52.3	2.7
Orientated 2nd Pass	-	0.1	0.3	8.5	31.9	57.1	2.1
Hand-Fed 1st Pass	-	-	0.6	12.0	39.7	47.5	0.2
Molded Sheet	-	-	0.4	10.6	32.0	54.9	2.2

Wet Premix - 60/40 Glass/Epoxy  
 Original Glass - Classified Flake (+8 Mesh)  
 Vacuum Blended Total Time 17 min.

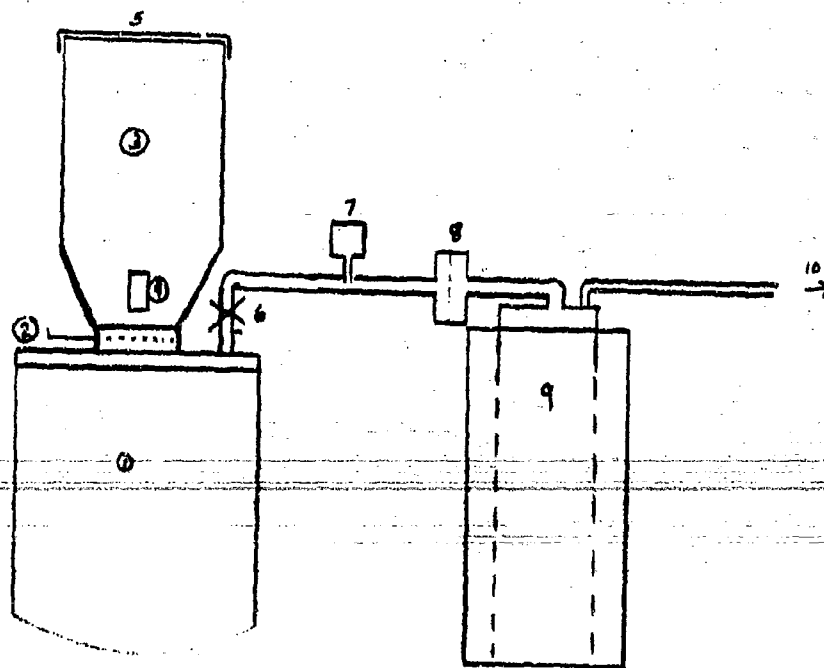
58.4  
 58.0  
 58.6  
 58.4  
 58.5  
 57.9  
 57.2

TABLE 7

Glass Breakdown Study  
60/40 Vacuum-Hopper Blend

Screen Mesh	% +4	% +8	% +16	% +30	% +50	% +100	% Pan	% Loss	% Glass
Original Glass	71.0	15.1	6.9	1.9	1.1	1.1	0.8	2.1	100
Wet Premix	-	-	0.1	1.0	21.6	35.6	39.2	1.6	60.1
Oriented 1st Pass	-	-	0.10	2.0	21.3	35.6	39.1	1.9	60.0
ELR-3-14	-	-	0.03	2.0	22.0	35.0	40.0	1.0	59.5
			Trace						



Sketch 1Abbe Mixer with a Vacuum Hopper

1. Abbe mixing chamber
2. Hopper-mixing chamber seal
3. Hopper
4. Sight glass
5. Hopper vacuum lid
6. Valve
7. Vacuum gauges
8. Screen pack
9. Dry ice vapor trap
10. Vacuum pump

The bridge was broken and the remaining glass added to the batch. The mixing time was determined with a stop watch and only the time that the mixer blades were moving was recorded. A total time (from introduction of the first flake up to complete glass flake wet-out and mixing) of 19 minutes was required.

The blend was removed from the mixer, processed through the calender-orientation assembly, molded and machined into the proper size physical test specimens.

The glass flake size distribution of the original unmixed glass, the blended premix, the oriented uncured sheet and the laminate was determined.

The data presented in Table 7 is compared with similar data obtained from materials processed by other techniques, in Table 8. Examination of Table 8 shows that although the blending under vacuum required approximately 19 minutes of mixing to obtain proper wet-out, only 2.0-2.1% glass flakes was retained on a +30 mesh screen. The data (in Table 8) indicates that although some decrease in glass flake breakdown was realized utilizing vacuum blending, the effect of this increase (from 0.5-1.9%) upon the molded laminates will be slight.

The vacuum apparatus requires several mechanical modifications to optimize its usefulness, including a method of preventing glass flake "fines" from the vacuum pump, and a means of eliminating the bridging of glass flakes over the hopper opening. The highly abrasive glass flakes can cause major mechanical damage to a pump if they are permitted to enter the mechanism. Screen packs are not an effective separation device. Bridging over of the hopper-mixing chamber opening must be eliminated.

Use of vibrators or pulsating fluted rods at the orifice can prevent the formation of the bridge.

The time required to obtain a uniform premix is 17-19 minutes versus 30-35 minutes for atmospheric blending, but the shorter mixing time is still longer than the critical time period which is less than 10 minutes of the Abbe mixing. The critical time period, discussed in detail later on in this report, is the mixing time which will keep the glass flake breakdown from going below a 20 per cent retention on a 30 mesh screen.

Therefore, because significant increase physical properties were not obtained from the specimens prepared through this technique, additional vacuum hopper runs were not run.

#### IV.3.2.1.4. Conclusions

Abbe mixing is a simple and effective method of blending resin and glass flakes. Uniform glass wet-out and resin flake distribution throughout the premix is obtained. Vacuum blending in the

TABLE B

## Effect of Blending Method Upon Flake Size Distribution

Screen Mesh	% +4	% +8	% +16	% +30	% +50	% +100	% Pan	% Loss	% Glass
Original Glass									
X	71.0	15.1	6.9	1.9	1.1	1.1	0.8	2.1	100
Y	-	73.6	11.5	5.1	6.0	2.9	2.0	2.0	100
Z*	70.7	14.6	8.5	1.8	1.3	0.5	0.4	2.1	100
	54.2	20.4	11.0	3.4	4.6	3.4	1.7	1.3	100
Wet Premix									
X	-	-	0.10	1.9	21.6	35.6	39.2	1.6	60.1
Y	-	-	0.10	0.5	14.5	35.4	47.6	1.9	58.4
Z	-	-	trace	0.6	18.1	38.3	42.5	0.5	59.8
Oriented 1st Pass									
X	-	-	0.10	2.0	21.3	35.6	39.1	1.9	60.0
Y	-	-	-	0.4	10.2	34.4	52.3	2.7	58.4
Z	-	-	-	0.8	22.7	39.3	36.7	0.5	60.0
Molded Sheets									
X (ELR-3-14)	-	-	trace	2.0	22.0	35.0	40.0	1.0	59.5
Y	-	-	-	0.4	10.6	32.0	54.9	2.2	57.2
Z (ELR-3-5)	-	-	-	0.4	12.4	38.1	47.6	1.50	60.4

X = Vacuum Hopper

Y = Vacuum Bulk Addition

Z = Atmospheric Addition

Total Mixing Time, Min.

19  
17  
30-35

\*2 Boxes of Original  
Flake used

Abbe mixer reduces blending time. There exists an optimum mixing range (15 to 30 minutes) below which resin coating on glass flake is insufficient and beyond which excessive breakdown is experienced. The Abbe mixing process is not as degrading to glass flake size as the other processes evaluated; however, breakdown of glass is a limiting factor in the utility of this process.

Large batch sizes or higher glass flake contents increase the rate of flake degradation. Glass flakes must be added slowly to the Abbe. Rapid or batch addition increases flake degradation. The larger glass flakes disappear from the premix rapidly because of selective attrition of the largest flakes. Vacuum blending requires the use of effective glass flake and "fines" filtering to prevent entrance of the destructive glass into the vacuum pump.

#### IV.3.2.2. Dry Blending Technique

The original study was performed with solid resins. The techniques developed in these studies were then used to prepare the phenolic-glass flake resin systems described in detail further on this report.

Formulations E-10, Table 9 and E-15, Table 10, were B-staged by allowing the resin batch to solidify at room temperature for a period of 24 hours. The resulting B-staged polymer was powdered in a Bantam Size Micropulverizer. All pulverized material passed the 0.020 inch Herringbone Classifier Screen in the pulverizer. The resulting powder was blended with 50 weight per cent of glass flake in a 5000 ml. glass finned flask rotating at 20 rpm for a period of one hour, at which time the flakes appeared well coated. In Table 9 are listed the details of this experiment. Although several laminates were prepared, only a small number were suitable for testing.

It should be noted that after dry blending, the flake resin composite retained the low weight to volume ratio (0.05 grams/cc.) that the flake originally had. Therefore, compression molding several inches of this material directly after tumbling results in a very thin laminate. After producing E1-10-1, some material was tested to see whether cold preforming (Munton Hydraulic Ram System 2" preform diameter) of this bulky mixture would reduce its bulk factor; however, crushing of the flakes occurred (at 500 psi).

Glass flakes were charged into a Patterson-Kelley blender (commonly known as a V-blender) Photograph 1, and tumbled for a period of one-half hour. The action of particle to particle causes a static charge build-up on the glass. Either a B-staged pulverized solid resin and a pulverized hardener is then charged to the blender. The materials then are blended for two hours. This method has been used for the formulation of glass contents of 50, 60, 70 and 80% glass.

Tensile strengths are reported in Table 10 at the 50% glass content studied. Thin laminates were produced at various curing

TABLE 9

## Compression Molding of Dry Blend

Laminate EL-10-1

## Procedure:

1. Dry blend for 1 hour
  - 50 wt. percent 2 micron unclassified glass flake
  - 50 wt. percent E-10 micropulverized resin
2. Compression mold for 1 hour at 300°F
  - 10" x 10" Elmes Press
  - contact pressure used

## Laminate:

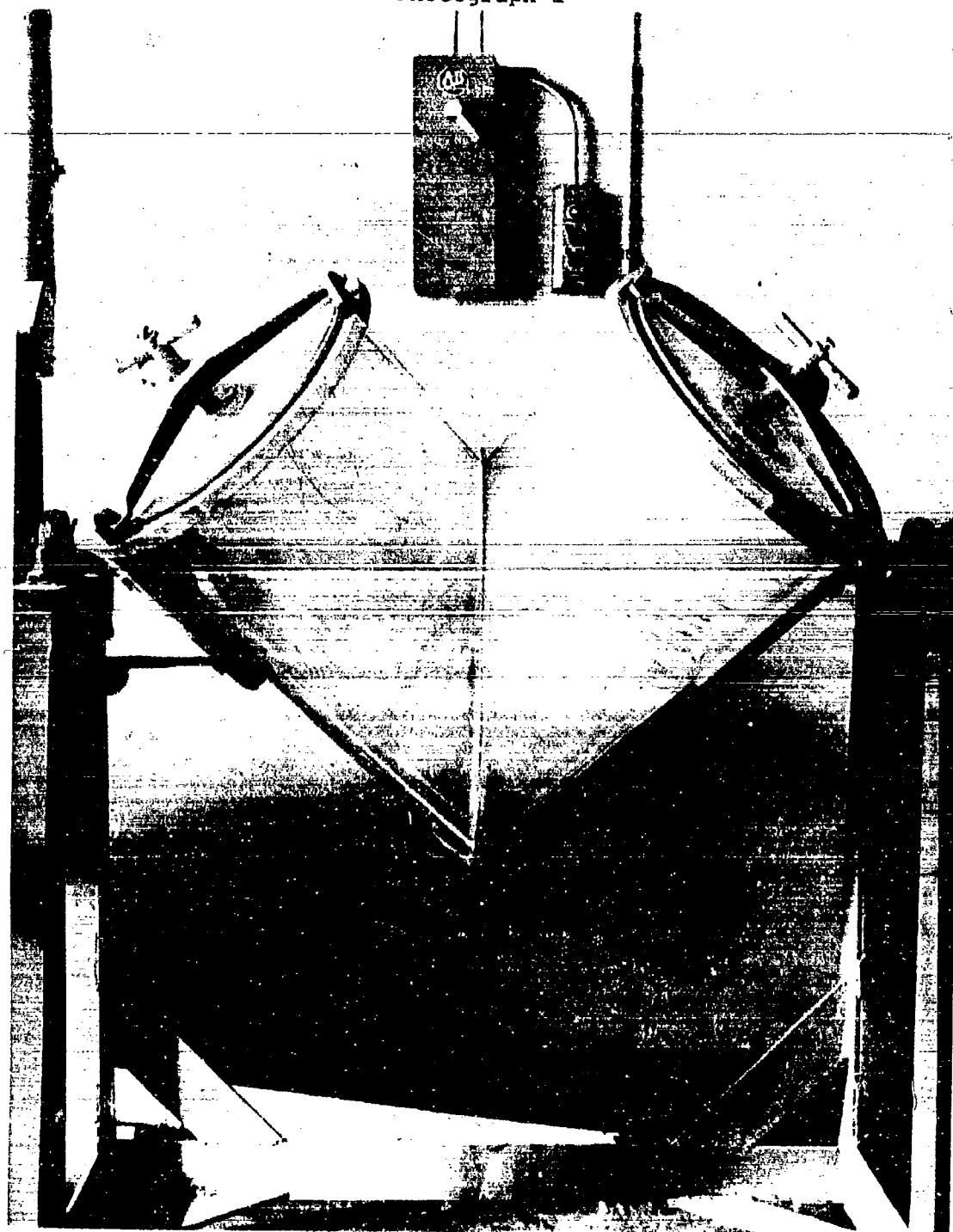
1. Dimensions 0.060" x 6" x 8" approx.
2. Appearance - air bubbles present
  - some limited flow patterns of resin

T A B L E 10

**PHYSICAL PROPERTIES OF LAMINATES PREPARED BY DRY BLENDING**

Laminate Identification	Resin Formulation	Initial Content		Glass Size	Mixing Method	Cure Cycles			Laminate Properties			Tensile Strength		Tensile Modulus			
		g.	Wt. %			Step	Time Hrs.	Temp. °F.	Press. psi	Thickness Inch	Density Gr/cc	% Glass	% Voids	x 10 <sup>-3</sup> psi		x 10 <sup>-6</sup> psi	
														Average	Range	Average	Range
EL-15-2	510 MPD	100 14	50	U	D	1	1	320	C	0.085	1.57	-	12.8 16.4	4.30 16.4	5.94 6.88		
EL-15-3	510 MPD	100 14	50	U	D	1	1	450	C	.180 .183	1.56	36 47.2	10.9 11.5	10.6 11.5	3.80 3.58		
EL-15-4	510 MPD	100 14	50	U	D	1	1	350	C	.073 .076	1.56	38 46	14.8 17.8	13.1 17.8	3.37 3.85		
EL-15-5	510 MPD	100 14	50	U	D	1	1	500	C	.074 .079	1.52	39	8.65 11.0	7.20 11.0	-		
EL-15-6	510 MPD	100 14	50	-8 M +16M	D	1	1	500	C	.065 .071	1.5	46	8.39 10.90	6.14 10.90	2.19 2.52		
EL-15-7	510 MPD	100 14	50	-8 M +16M	D	1	1	450	C	.125	-	-	6.12 7.30	4.95 7.30	3.92 5.26		
EL-15-8	510 MPD	100 14	50	-8 M +16M	D	1	1	350	C	.090	1.387 1.384	47.3 47.1	8.78 9.40	7.75 9.40	2.38 2.94		

Photograph 1



Patterson-Kelley Blender

cycles. For the resin system studied, a 350°F cure temperature optimized tensile strength properties using 50% unclassified glass as indicated in Figure 4.

Analysis of the dry blends revealed a 3-12% variation in glass content, although the batch was prepared with a 50% glass content. Sampling individual sections of a given laminate points out these glass variations. All laminates prepared, using any of the blending techniques, exhibit this phenomenon. The variation in glass content occurs during molding, resulting in point to point variations. This may be one of the reasons for wide variations in tensile strengths of all tested samples. The "clumping" or glass segregation occurred because a confined compression mold was not used. Compression molding between chrome plated caul plates, using stops, does not sufficiently confine the laminate during curing. Resin drain-out was observed even at contact molding pressures.

Computed tensile moduli at the 50% glass content for dry blended laminates range from 1.60 to 6.88 million psi. Flexural strength of these dry blends varied from 9.9 - 16,700 psi, with an average modulus of 2.4 million psi. Flexural data is contained in Table 11. Void percentages (Table 10) as calculated are low, giving credence to the higher tensile values obtained.

Hot preforming of the dry blended compounds has been accomplished by subjecting it to a 190-200°F temperature for a short time under low pressure, followed by rapid cooling. Molding several of the pre-forms in a compression press has resulted in fabrication of a 0.180 thick sheet. Even after hot preforming, the precured apparent density is only approximately 25% of the final cured density of the laminate. It is expected that dry blends could be used for filling intricate, thin-walled cavities. Large daylight area presses would be required for the molding of thick-walled sections.

#### IV.3.2.2.1. Conclusions

Tumbling glass flakes with either a catalyzed or uncatalyzed resin dust is the main principle involved in dry blending. Static charges developed during blending of the glass and resin aid in the obtainment of a uniform resin coating on each flake. Catalyzed, B-staged pulverized resins are preferable because of the shorter time required to cure them to a hardened laminate. Only a small amount of glass flake breakdown occurs during this process.

#### IV.3.2.3. Plenum Chamber Process

The plenum chamber process incorporated coating airborne glass flakes with a fine mist. The salient feature of this process is that it readily lends itself to continuous production.

The plenum chamber used was a 4' x 4' x 8' sheet metal chamber with six separate sliding hole mounts for the Paasche airbrushes. The airbrushes could be raised or lowered to give any desired spray



Figure 4

38.

Tensile Strength  
vs.  
Cure Temperature

Dry Blends EL-15-2, 3, 4, 5

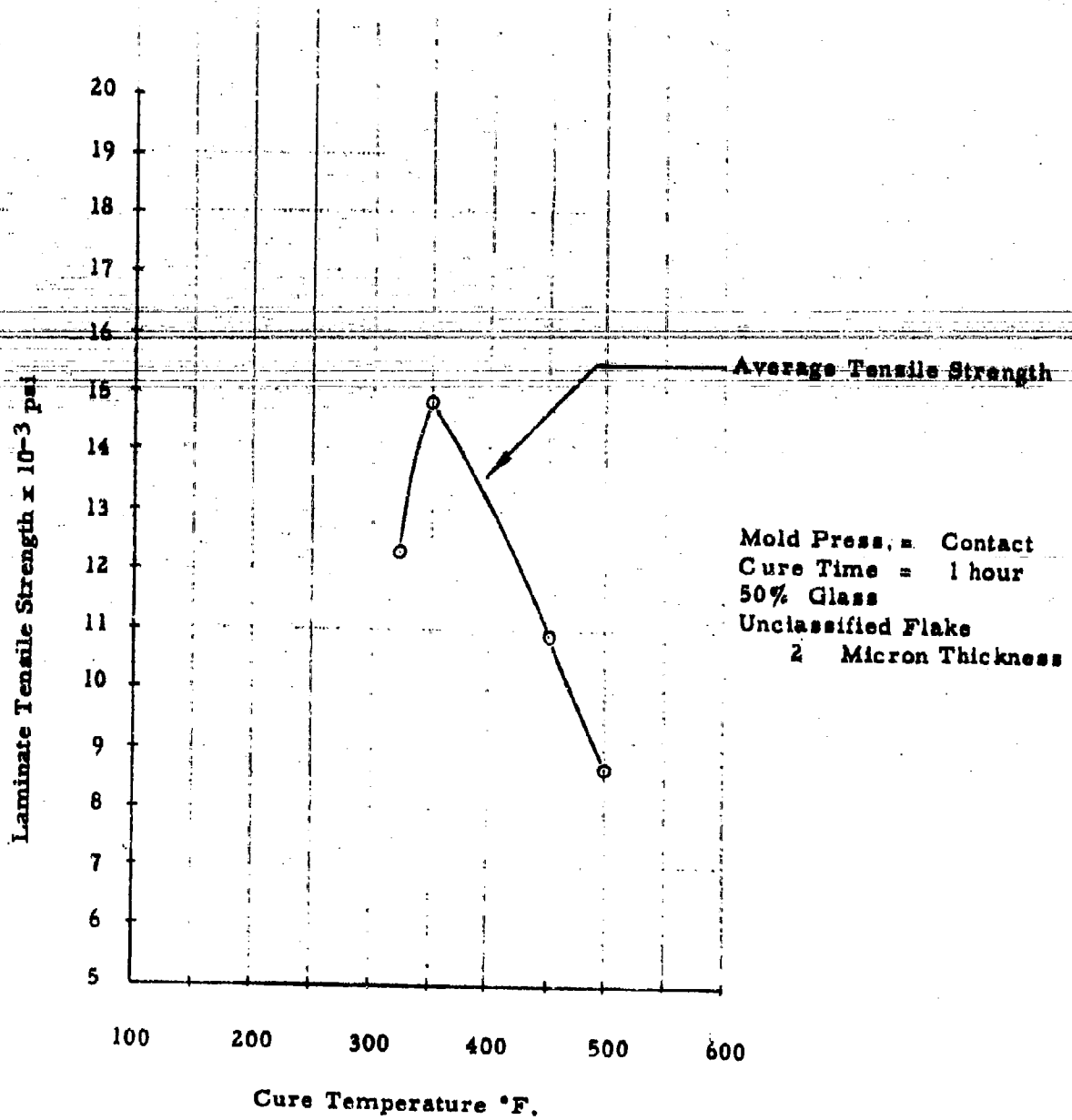


Table 11

## Flexural Strengths of Laminates

Prepared by Dry Blending Method

Laminate Identification	Flexural Strength psi $\times 10^{-3}$		Flexural Modulus psi $\times 10^{-6}$	
	Average	Range	Average	Range
EL-15-4	14.8	9.9-16.7	2.40	2.3-2.5
EL-15-7	11.3	10.1-12.8	2.37	1.33-4.02

level in the chamber. (Photograph 2.) The plenum chamber was designed to allow venting of the air pressure through a filter sock rather than a screened section of the conveyor pipe for glass flake.

Calibration of the resin delivery system, Paasche airbrushes, and glass flake delivery from the Agile Cloud Chamber was required before glass-resin mixtures could be made. This process was a multi-stage batch process. Since most of the samples required by the programs were relatively small, no attempt was made to adapt this step for continuous production until its usefulness and effectiveness had been proven.

The plenum chamber process had undergone extensive development from that used in previous studies. Initial trials were conducted using air atomized resins to coat glass flakes which were air blown into the plenum chamber.

The use of liquid spray resin atomizing system showed a definite improvement over the operation observed when an air gun was used to atomize the resin-hardener system. Atomization of epoxy resins into a fine mist was accomplished by use of 1000-2000 psi pressure developed on the resin before passing through a liquid atomization nozzle (Spraying Systems Co. No. 950LTC, Orifice size 0.0135 in.). Resin delivery rates observed were 200/gm/minute. Use of the very viscous epoxy resins resulted in excessive foaming of the resin at the liquid nozzle.

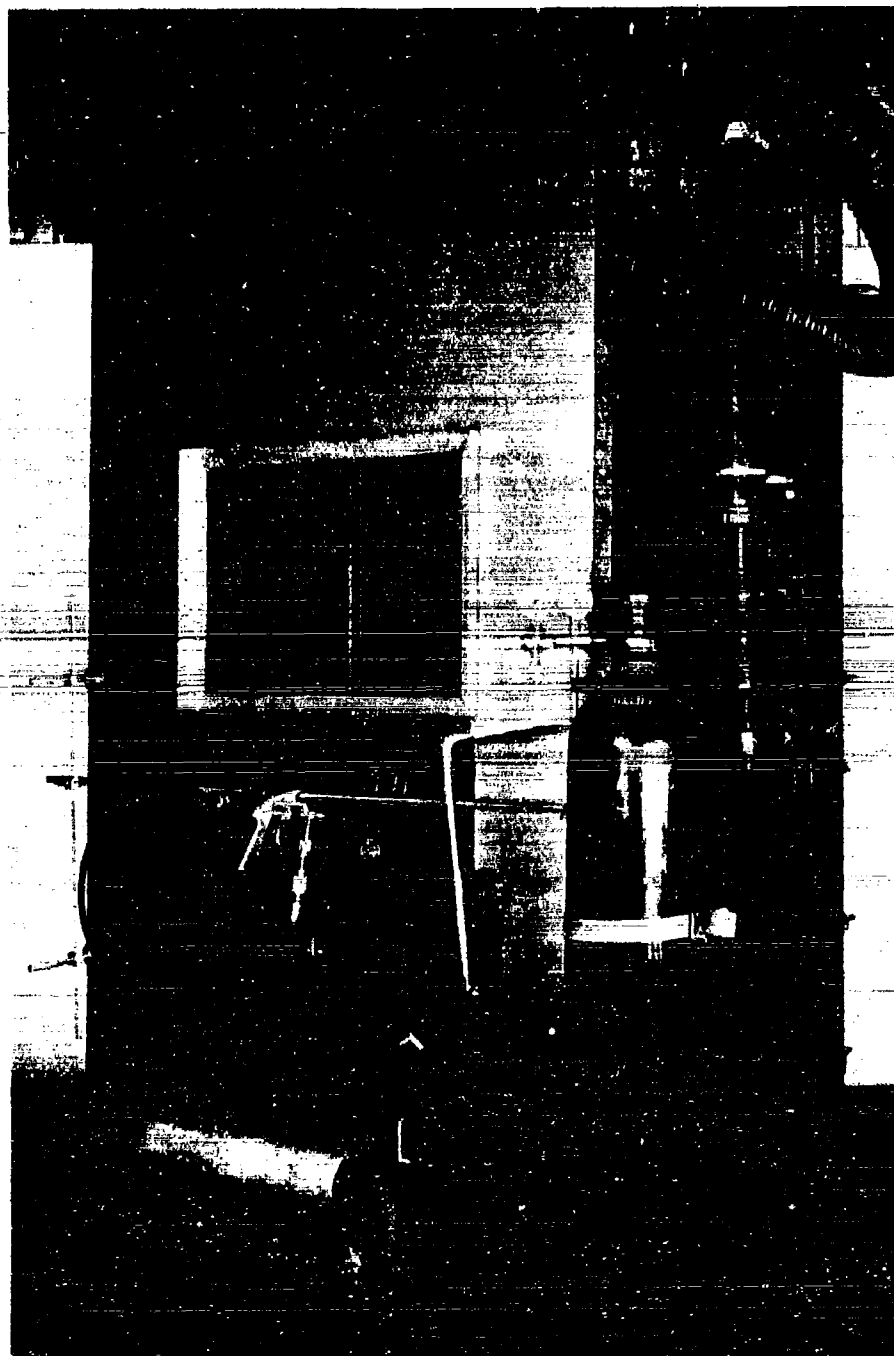
Wetting of glass flake in the plenum chamber, using a liquid epoxy spray, was more complete than when air was used for atomization. No turbulence was encountered when the liquid spray was used. Resin wet glass flakes prepared in the plenum chamber, using the liquid spray system, still had excessive amounts of air inclusions and non-homogeneous wetting of glass flakes was observed due to uneven glass flake delivery using the Agile cloud chamber.

A star valve and hopper was designed, fabricated and installed above the plenum chamber. Their purpose was to accurately meter glass flake and deliver the flake by gravity into the resin mist. Static tests of this star valve metering unit were hindered by bridging of the glass flake in the hopper throat just before entry into the star valve. A bridge breaking device was installed and eliminated this problem.

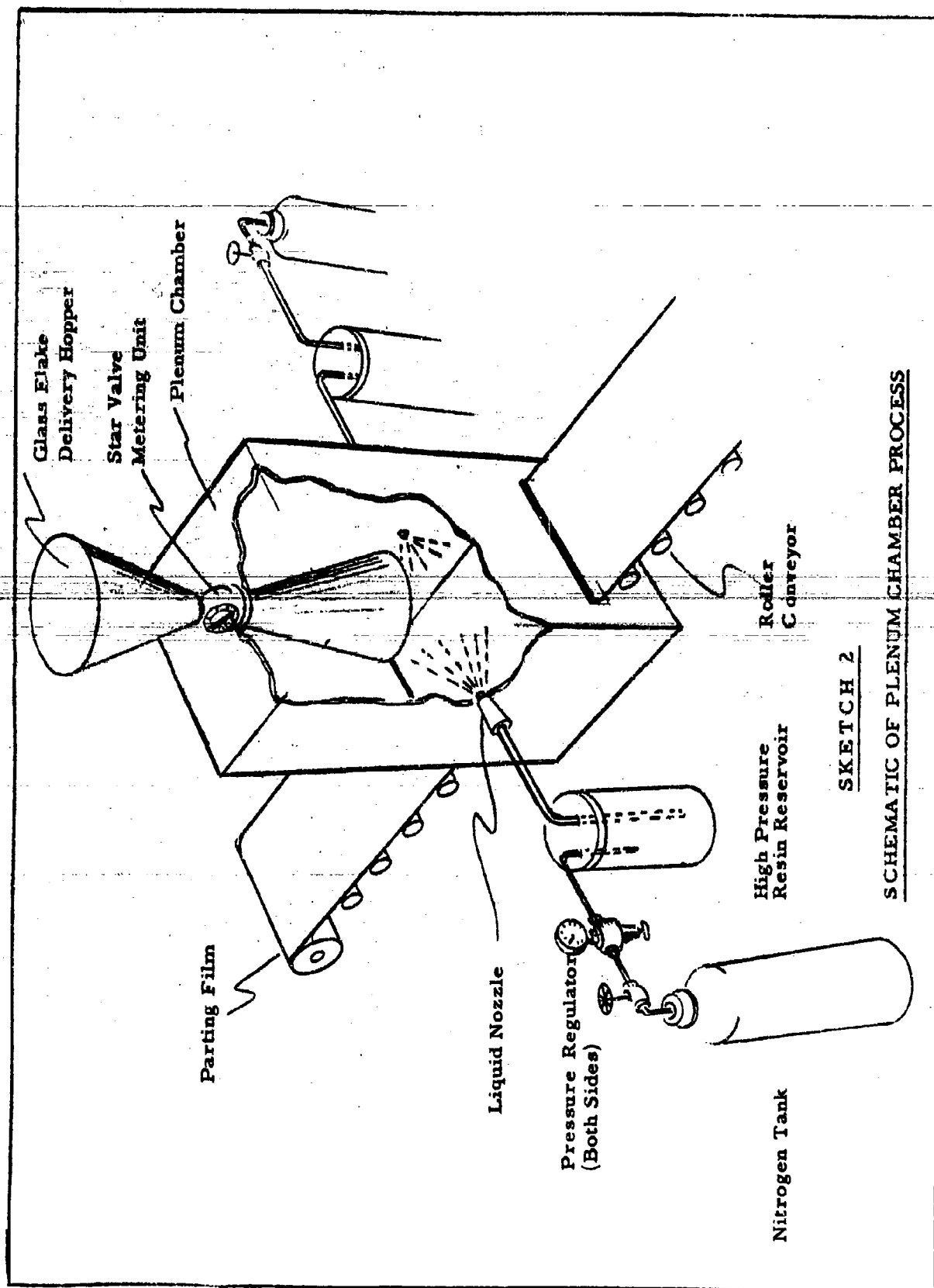
#### IV.3.2.3.1. Conclusions

Sketch 2 is a process schematic of the plenum chamber operation. All laminates produced with this process have exhibited variations of resin and glass composition within a laminate. Unstable operation in the plenum chamber was responsible for this. Table 12 lists the typical properties obtained from laminates prepared with plenum chamber mixed systems. As can be seen, the physical properties of the laminates were generally poor. The low values can be

Photograph 2



Plenum Chamber Assembly



SKETCH 2

SCHEMATIC OF PLENUM CHAMBER PROCESS

Table 12

**Physical Properties of a Typical Laminate  
Prepared by the Plenum Chamber Process**

<b>Laminate</b>	<b>EL-16-2-5</b>	
<b>Formula</b>	<b>UNOX 207</b>	<b>100</b>
	<b>Maleic anhydride</b>	<b>73</b>
	<b>Trimethyl propane</b>	<b>10.6</b>
<b>Blend</b>	<b>50% unclassified flake</b>	
<b>Cure Cycle</b>	<b>1 hour at 320°F and 0 psi pressure</b>	
	<b>6 hours at 400°F and 0 psi pressure</b>	
<b>Laminate Thickness</b>	<b>2.11 - 2.15 inches</b>	
<b>Density</b>	<b>1.40 Gr/cc</b>	
<b>Glass content</b>	<b>31 - 38%</b>	
<b>Void content</b>	<b>13%</b>	
<b>Tensile strength</b>	<b>average 3.36 x 10<sup>3</sup> psi</b>	
	<b>range 2.24-4.54 x 10<sup>3</sup> psi</b>	
	<b>Tensile modulus 2.06 x 10<sup>6</sup> psi</b>	

explained by stating that laminates prepared from plenum chamber blended materials exhibited resin rich and resin dry areas, large amounts of entrapped air bubbles and many areas of disorientation of glass flakes.

Many of these problems could be eliminated if the proper further processing, such as calender orientation and vacuum treatment, were used - but the problem on non-uniformity of glass content would not be aided. In addition, it should be noted that the plenum chamber requires large volumes of excess resin to wet out the flake. This resin is squeezed out during the molding cycle.

#### IV.3.2.4. Solvent Coating Techniques

Throughout the program there existed a definite need for refined solvent coating methods usable for glass flakes. Two areas of importance are: (1) coating glass flakes with bonding agents, and (2) coating glass flakes with high-strength solid resins to obtain higher glass contents than those presently available without degradation of glass flake size. A bonding agent should improve the strengths of polyester-glass flake laminates which have been lower than the strength of the resin itself. We believe that this abnormality was caused by poor chemical bonding between glass flake and the polyester resin and poor cohesion of the resin binder system.

In order to upgrade the strengths of glass flake reinforced laminates bound with polyester resins, the technique of coating glass flakes with Union Carbide's A-1100 silane coating agent was evaluated. Glass flakes were charged into the Abbe mixer which contained 1% water solution of the glass bonding agent. The temperature of the mixture was held at 190°F for a one-hour period, as recommended by Union Carbide. The large excess of water was drained from the glass flakes and, subsequently, the flakes were placed in an air-circulating oven at 250°F for a period of six hours to remove as much of the water solution remaining on the glass flakes as possible. Thereafter, 50-100 gram batches of the treated flake were placed in the dielectric heater where remaining traces of water were volatilized.

The A-1100 treated batch of glass flakes was then used to prepare a laminate using American Cyanamid's polyester resin Laminac 4128 catalyzed with 2.0% benzoyl peroxide. The resultant laminate was of decidedly poor quality and was not tested. Evidently, segregation of the A-1100 silane finishing agent on the glass flakes caused localized curing reactions. Laminate quality and density varied from spot to spot within the laminate.

Solvent coating of solid resins to glass flake was investigated. It is well known that many commercially available solid epoxide resins have inherently higher physical properties than commercial liquid epoxy resins. However, the method required to combine these solid resins with reinforcing materials is necessarily more complicated than the technique used to combine liquid resins with reinforcing materials. An approach taken to combine the solid resin

with glass flake was in accordance with the solvent coating technique. A large excess of solvent (acetone) was used to dissolve Epon 1031 (Shell Chemical Co.) and the hardener, methyl Wadic anhydride resin. The resultant solution (17% solids) was used to coat the glass flakes in the Abbe mixer. Drainage of excess solvent followed by oven exposure and dielectric heating was used to remove solvent from the glass flake. A thin laminate sheet was compression molded from the dry mixture of the coated glass flakes. Molded appearance revealed the presence of dry glass flake in patches where, evidently, resin had been "washed" off the flakes during removal of excess solvent. Continued efforts to use this technique for coating glass flakes were unsuccessful.

(The solvent-resin coating system has been used commercially to produce shellac-mica flake laminates. The physical properties of these laminates is unknown.)

#### IV.3.2.4.1. Conclusions

The process solvent coating is of potential value, but the effort required to reduce it to usefulness will be extensive and may prove uneconomic.

Unevenness of resin coating on glass flakes resulting in resin rich and resin starved areas. Difficulty in removing all traces of solvent without overcuring the reactive resin system. This system may be used if thermoplastic resin binders are to be used. Binding of individual glass flakes into books or "plates" which are degraded during the molding cycle.

#### IV.3.2.5. Centrifugal Blending

The basic principle involved in the centrifugal process is the flow of resin from the center of a rotating centrifuge to the outer wall as a result of centrifugal force. As the resin seeks the maximum diameter, it comes into contact with glass flakes charged into the centrifuge at the start of the operation, and thereby "wetting" of the glass flakes is accomplished.

Although a basic advantage realized, using this process, is accurate, control of the charge ratios of glass and resin since it is a batch process, a disadvantage is that mixing times required have been one hour for 200-400 gm. batches. Even at the one-hour mixing times, insufficient wetting of the glass, flake clumping, and inclusion of air pockets have been observed. The laminates prepared, using the centrifuge process for mixing glass flake with resin have not given outstanding tensile strength properties (3-10, 700 psi).

A 6-inch diameter cylinder mounted on a two-speed motor (1850 and 4800 rpm) was used for the centrifuge studies.

In Table 13 a summary is given of the laminates prepared from premixes made in the centrifuge; the processing data for the first centrifugal blend is shown in Table 14.



TABLE 13

## PHYSICAL PROPERTIES OF LAMINATES PREPARED BY CENTRIFUGAL MOLDING AND THE PLENUM CHAMBER

Laminate Identification	Resin Formulation	Initial Content Wt. %	Glass Size	Mixing Method	Cure Cycles			Laminates Properties		Tensile Strength		Tensile Modulus						
					Step	Time Hrs.	Temp. °F.	Pressure psi	Thickness Inch	Density Gr/cc	Glass Voids %	x 10 <sup>-3</sup> psi		x 10 <sup>-5</sup> psi				
												Average	Range	Average	Range			
EL-14-2-1	JD 510 HHPA DMP-10	100	50	U	C	1	5 min	325	1000	.270	1.72	70	9.60	8.30	11.5	-	-	
		50	2			2	325	300										
EL-16-2-1	U 207 MA TMP	100	50	U	C	1	21	225	400	.191 .196	1.71	71	5.25	4.84 6.66	8.15	6.30 9.12	-	-
		73	2			1	320	0										
EL-16-2-2	U 207 MA TMP	100	50	+8M	C	1	1	320	200	.200	1.44	47	4.00	3.17 4.62	5.98	4.84 6.66	-	-
		73	2			6	400	0										
EL-16-2-3	U 207 MA TMP	100	50	-8M +16M	C	1	1	320	500	.132 .144	1.44	53	7.86	4.42 9.60	8.50	6.20 9.90	-	-
		73	2			6	400	0										
EL-16-2-4	U 207 MA TMP	100	50	-16M	C	1	1	320	500	.174 .184	1.90	72	7.65	5.5 10.7	5.40	5.38 5.42	-	-
		73	2			6	400	0										
EL-18-1	JD 504 HHPA DMP-10	100	50	U	C	1	2	300	500	.139 .144	1.76	66	9.01	7.52 10.5	8.60	-	-	-
		50	1			2	300	500										

Key to Table 13FormulationsEpoxide and di-epoxide resins

JD510 - Epi Rez 510 - Jones Dabney Co.

JD504 - Epi Rez 504 - Jones Dabney Co.

U207 - Unox 207 - (di-epoxide resin) - Union Carbide Plastics Co.

Curing Agents

HHPA - Hexahydrophthalic anhydride - National Aniline Div. - Allied Chemical

DMP-10 - Accelerator - Rohm and Haas Co.

MA - Maleic anhydride - American Cyanamid

TMP - Trimethylol Propane - Heyden Newport Chemical Co.

Initial Glass Content

Refers to weight per cent of glass flake charged

<u>Initial Glass Size</u>	U	-	unclassified
	+8	-	retained on 8 mesh screen
	-8	-	passing through 8 mesh
	+16	-	retained on 16 mesh screen
	-16	-	passing through 16 mesh screen

Cure Cycles

Pressure, psi C - Contact pressure used during cure

Tensile Strength

Tensile strengths determined in accordance with ASTM D638 - 58T

Flexural Strengths

Flexural strength performed in accordance with ASTM D790 - 58T

# Compression Molding of Centrifuge- Produced Blend

## Procedure:

1. 282 grams ungraded E-glass-flake  
282 grams E-12 resin
2. Resin and glass admitted periodically into  
centrifuge; 20 minute mixing cycles; remove  
resin-wet mix from centrifuge walls and remix
3. Total mixing time - 1 hour
4. Resin temperature during mixing - 65°C

## Cure:

1. 10" x 10" Elmes Press
2. Contact pressure to close
3. 200°F 1 hour  
250°F 16 hours  
at 500 psi
4. Resin drainoff during cure

## Laminate:

1. Dimensions 0.183" x approx. 7" x 7"

## Properties of Cured Laminate:

Sample	Tensile Strength psi	Average Tensile Modulus
1	6,800	
2	8,050	3.63 x 10 <sup>6</sup>
3	11,800	

Glass Content  
before molding  
50%

after molding  
78.5% Average

Molded Density  
1.86  $\frac{\text{grams}}{\text{cc.}}$  average

Gas Occlusion volume %  
approximately - 14

Glass flake was charged into the vertical centrifuge; thereafter, catalyzed resin was added at the center and rotation of the bowl begun at 4800 rpm to promote quicker mixing through resin flow. This process was developed in previous Olin contract 6.

Mixing times were one hour with stops at 15 minute intervals to remix the high resin content glass mixture which had segregated to the maximum diameter of the centrifuge, back to the center of the centrifuge. The time required for the remix step was one minute.

Inasmuch as mixing times are one hour, an alternate resin system was chosen which had lengthened pot life at room temperature and also a low fluidity or viscosity. The formulation used was Unox 207, a di-epoxide.

#### IV.3.2.5.1. Conclusions

Laminate properties for laminates made with centrifugally prepared premixes appear in Tables 14 and 15 and compared with other materials in Table 16. It should be noted that various degrees of resin squeeze out occurred giving 31-72 weight per cent glass in the final laminate.

Generally, laminate strengths are low; laminates produced were misoriented and contained voids. Average 1 minute tensile strengths varied from 4 to 11,800 psi at varying glass content.

The long blend time required to obtain a complete and uniform mix combined with the difficulty in preparing blends with glass flake concentration above 50% caused us to terminate this phase of the program. We believed that continued efforts would not yield an economic and reproducible process.

#### IV.3.2.6. Two Roll Milling

Attempts at using a 2-roll mill as a means of blending glass flake with resin were unsuccessful. The resultant premix was noticeably inferior and contained a much higher "fine" content than those produced by other blending methods evaluated.

A small quantity of fluid catalyzed resin was poured onto the moving 2-roll mill. The nip clearance was reduced to a minimum to prevent excessive resin drip from the rolls. The glass flakes were slowly sprinkled onto the moving roll until all visible resin is absorbed. The process of alternately adding resin and flake is continued until all the ingredients were blended.

"Wet out" of the flakes by the resin became increasingly difficult as the batch size was increased. Excessive glass flake breakdown was noticeable almost immediately.

#### IV.3.2.6.1. Conclusions

The 2-roll milling of glass flake is a poor means of combining flake with resin. The dry, brittle glass flake is subjected to high

Table 15

**PHYSICAL PROPERTIES COMPARISON  
CENTRIFUGAL BLENDED SYSTEMS**

	<u>Glass Flake Laminate</u>	<u>Plain Low Carbon Steel</u>	<u>Heat Treated Special Alloy Steel</u>
Specific Gravity	1.68	7.98	7.98
Density, lb./cu. in.	0.061	0.283	0.283
Tensile Strength psi	11,500	40,000	240,000
Modulus of Elasticity, psi	8,600,000	30,000,000	30,000,000
Strength to Weight Ratio:			
( <u>Ultimate Strength</u> ) (     Density     )	209,000	138,000	828,000

TABLE 16

PREFORM STUDY OF RESIN-WET EPOXY PREMIXES

	Procedure	P R E F O R M			C O M M E N T S
		Temp. °F.	Press.	Time Hrs.	
PF-1	1	200	200	1 1/2	Sheet rigid - Cure advanced too far
PF-2				1 1/4	Sheet rigid - Cure advanced too far
PF-3				1 hr. 5 min.	Sheet rigid - Cure advanced too far
PF-4	2	200	200	1 hr.	Sheet undercured - Stuck to mold
PF-5				55 mins.	Sheet undercured - Stuck to mold
PF-6				50 mins.	Sheet undercured - Stuck to mold
PF-7	3	200	200	1 hr. 5 min.	Preform tested for rigidity during cure - Good sheets
PF-8				55 min.	Preform tested for rigidity during cure - Good sheets

shear when it passes through the narrow gap between the rolls. A very rapid (glass flake) degradation rate is experienced.

The 2-roll milling process exhibited an interesting phenomenon in that flakes in the mass after complete blending apparently became oriented. It was this observation which lead to the construction and evaluation of the other calender process system.

The rate of flake degradation experienced in 2-roll blending is increased as the glass flake content is increased. Most blends were evaluated at a 50% glass flake content. It was noticed that as the last of the glass was added degradation increased rapidly. This increase was accelerated if the glass flake content of the mixture was in the range of 60% or 70%.

#### IV.3.3. Premix Processing

In preparation of laminates evaluated early in this program, great difficulty was encountered in obtaining specimens free of internal flaws. It was decided to develop intermediate processes for conversion of premixed flake-resin systems into moldable forms. It was expected that resin flow, air entrapment, glass disorientation, and resin wet out problems could be relieved somewhat by such processing. To this end, processes for preform preparation, calender orientation, dielectric preheating, extrusion and injection molding were evaluated. Excellent results were obtained when wet premixes were processed by calendering, and good laminates were made from dielectrically heated preforms of dry blends.

#### IV.3.3.1. Preforming of Premixes

The preparation of cured glass-laminate sheets in thickness up to two inches, was difficult. Proper orientation of the glass flake, removal of the occluded gas, and uniformity of cure in a single molding operation were not obtainable. It was correctly postulated that thin, well-oriented and partially cured (B-staged) sheets could be stacked in layers, pressed together. Pertinent detailed data related to the initial formulations and procedures studied are given in Table 16.

The epoxy-acid anhydride system at 200°F. had an induction period of about 55 minutes to one hour before incipient cure started. Thereafter the curing rate was so rapid that the cure had advanced to an infusible state within 5 to 10 minutes. These sheets would not bond when stacked at a higher curing temperature.

Water cooling of the platens or cooling the mold in dry ice satisfactorily arrested the advancing cure. Both methods were usable, but the dry ice cooling method was more troublesome, and the preform was more difficult to remove from the mold.

Curing induction periods from batch to batch were variable. The proper control of handling and arresting the incipient cure of the EL-23 resin system (Table 17) required too much developmental attention to be considered further. An alternative approach using

T A B L E 17

DISTRIBUTION OF GLASS FLAKE IN  
CURED LAMINATE EL-23-2

Mesh Size	Premix Before Molding-After Mixing		Center Composite		C U R E D		S H E E T	
	Individual	Cumulative	Individual	Cumulative	Individual	Cumulative	Individual	Cumulative
8	0.7	0.7	0	0		0	0	0
16	3.0	3.7	0	0		0	0	0
30	27.8	31.5	2.3	2.3		2.3	0.2	0.2
50	30.3	61.8	44.0	46.3		46.3	29.8	30.0
100	29.1	81.9	27.3	73.6		73.6	33.6	63.6
Pan	16.5	98.4	24.2	97.8		97.8	35.7	99.3
Glass Content	60%		77.5%				79.7%	

## Resin Formulation:

Jones Dabney Epi-Rez 509 69.4 g. Epoxy Resin  
Methyl Nadic Anhydride 62.5 g. Curing Agent  
DMP-10 1.4 g. Accelerator

## Glass Content:

60% At Start  
+8 Mesh 2 Micron Glass Flake  
Final Glass Content: Determined at +1%

## Abbe Mix:

5 Mins. at 130° F.

Cure: Compression Molded. (0.100 in. thick)  
2 hrs. 200° F. 1000 psi  
2 hrs. 400° F. Oven



the wet resin system to B-stage the epoxy preforms with meta-phenylene diamine as a curing agent was then tried.

The technique developed was based on the preparation of the premix in an Abbe blender after which the wet blend was permitted to B-stage over a 24 hour period. The loose, bulky mass became a hard friable material which was broken by hand or chopped mechanically. It could then be charged into the preforming mold. The material was subjected to low pressures at temperatures slightly above the softening point of the resin binder system. The preform sheets which were formed were slightly oriented, low strength, poorly compressed laminates.

The preforms were then layered to produce laminates of the proper thicknesses in subsequent moldings. This system produced several disadvantages which resulted in discontinuation of this process.

The resin system (100 parts Epi Rez 510 and 14 parts meta-phenylene diamine) was also used to prepare the pulverized B-stage resin which dry blended with glass flakes. The higher degradation of flake size during Abbe mixing was established, as was the relatively low glass flake degradation resulting from dry blending of flake. Therefore, this process produced laminate with smaller flake size than the dry blending process. In addition, dry blending of the system subjected the glass flake to two less process steps.

The loose, non-oriented resin-flakes were charged into the heated mold cavity. The mold was closed and low pressure applied for limited periods of time. The variables of preform temperature, pressure and time were dependant upon the resin system used in the premix. Typical examples of various systems follow.

Table 18

**Preform Molding Parameters - Dry Blends**

<u>System</u>	<u>Temp., °F.</u>	<u>Time, Sec.</u>	<u>Pressure, psi</u>
Epoxy-Amine	160-170	15-30	200-250
Phenolic	270	5	200

Essentially minimum pressure, temperature and time required to compress, soften the resin, lightly bond and orient the glass flakes was used. There exists a moderate degree of freedom in choice of preform conditions, but too high temperature or pressure will result in sheets in which the resin is too highly cross-linked (cured) and therefore cannot be formed into laminates. Less than minimum preform conditions result in weak preforms that exhibit low cohesive strengths, poor orientation, little bulk compression and are difficult to handle.

#### IV.3.3.1.1. Conclusions

The preform process was used to process all the dry blended phenolic systems. Of the three premix systems preformed (wet premixes, wet premixes B-staged, dry blended systems) only the dry blended system was used in laminate preparation and evaluation. The wet premix systems are difficult to preform and present many difficulties, such as resin and glass flow during the longer preform process. The second method was effective but found to be far inferior to the calendering process which was subsequently developed, therefore it fell into disuse.

The dry blended preform is a low strength, friable, fragile, wafer which is still highly uncompressed. It was determined that if quality laminates are to be produced from dry blended systems, good preforms were necessary.

#### IV.3.3.2. Calender Orientation

##### IV.3.3.2.1. Prototype Evaluation

Calendering of dry blends and epoxy premixes was initially performed by depositing the premix in the nip of the 6 x 3 Farrel Birmingham 2-roll mill adjusted to rotate at 4 fpm. A parting film was used to prevent sticking of the premix to the calendering rolls. The premix was calendered between the parting film using cold rolls. Sheets that were produced in this manner were cured in an oven and molded in a compression press.

Sheets of various thicknesses were prepared. Sheet quality at a given thickness was dependent on glass content. The 40-50% glass content premixes formed oriented, smooth sheets. As the glass content was increased to 60%, the calendered sheet thickness delaminated immediately after calendering to a thickness larger than the rolls gap used. At these glass contents, it was noticed that the glass flakes did not adhere, allowing air voids to become dispersed into the sheet after calendering. Evidently at the lower glass contents of 45-50%, the surface tension and coverage of the resin hold the flake composite together.

Calendering development using the 6 x 3 Farrel Birmingham 2-roll mill was retarded because the 4 ft/min. calendering speed was too fast to allow required control of the sheet using our present premix systems. A hand operated 2-roll calender was constructed to allow calendering speeds which would be slower. The process consists of depositing a resin wet premix from the Abbe mixer on a carrier-parting film which passed through the nip of the calendering rolls adjusted to a desirable gap.

Using the new small calender, 0.004 in., 0.009 and 0.040 in. (thickness) sheets containing 50% glass with an epoxy binder were calendered and cured. A parting film of cellophane was used during the operation. The epoxy premix was not degassed, and as a result, the sheets formed had characteristic air inclusions. The calendered sheet expanded after leaving the nip of the rolls. The poor cohesion of the resin in the glass premix was responsible for the phenomenon.

In Table 19 the results are reported which were obtained when attempts were made to calender dry blended premix systems. The data shown indicates that calender-orientation of dry blends to be a feasible process. The calendered sheets were cohesive strips which were suitable for compression molding. This phase of the program was not continued because of limitations in the available equipment. (The 2-roll mill was not suitable for processing dry blends because of the relatively high speed of the rollers and the differential speed of the rollers. The work could not be continued using the new roller-orientation assembly because the rolls were wood and could not be heated.)

The combination of a low glass flake degradation resin blending process and orientation-compression process for dry blended mixes should be evaluated further. We believe that higher tensile values could be obtained if non-degraded flake were present in the laminates. This process combination offers an opportunity to obtain flake laminates of higher quality.

#### IV.3.3.2.2. Roller Calendering

The feasibility of orienting different thicknesses of sheet using the roller-calender and the effect of glass flake concentration upon process applicability indicated that roller calendering would be a suitable process for glass flake premixes.

Flat laminates and complex shapes have been molded from different thickness B-stage calendered sheets. A complete flake size distribution study using classified flake was then performed to evaluate process induced flake degradation levels. This study is presented later in this report.

The calendering orientation process produces flat sheet materials using the assembly illustrated in Sketch 3 and Photograph 3.

A modification of the above technique eliminated the use of the ram extruder feed mechanism to deposit the glass on the parting film. The loose non-oriented glass flake was hand packed on the conveyor-parting film. The flake was laid in a continuous strip 7"-8" wide and 1/4"-1/2" thick.

Flat oriented wet flake premixes which had been processed to 1/16" thickness were reprocessed through the roller assembly with reduced nip clearance to produce sheets as thin as 1/64" thick.

Many batches of epoxy-glass flake blended in glass flake concentrations of 50%, 60% and 70% have been processed by calendering. Batches of epoxy-glass flake (50/50) blends that have been processed by calendering into sheets of several thicknesses exhibited excellent orientation of the glass flakes. Laminates 0.150" thick have been produced from multiple layers of their calendered sheets which exhibited no visible signs of disorientation and no flow or knit lines. The laminates, exhibited the most transparency of any produced in this program.

Table 19

Two-Roll Mill Callendering of Dry Blends

## Procedure:

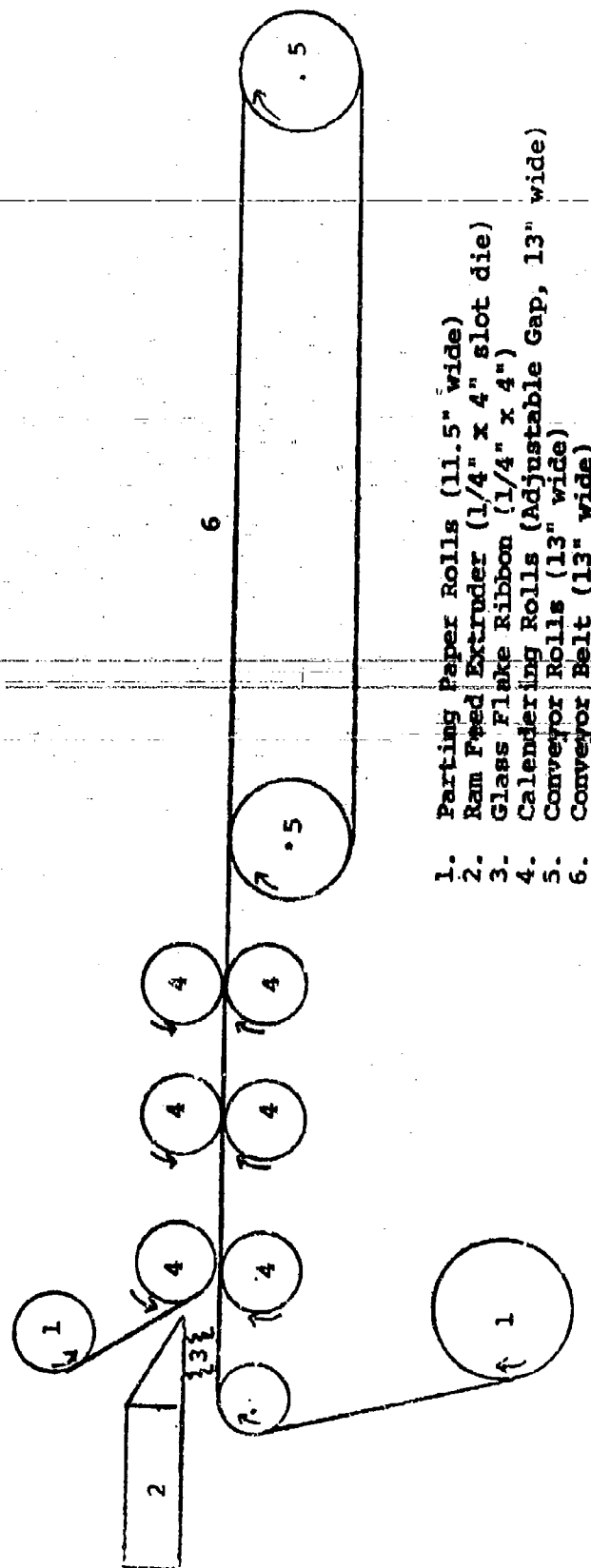
1. Use prepared blend E-10  
50 wt. % resin  
50 wt. % glass flake unclassified

## Equipment:

1. 6" x 13" Farrel Birmingham two-roll mill

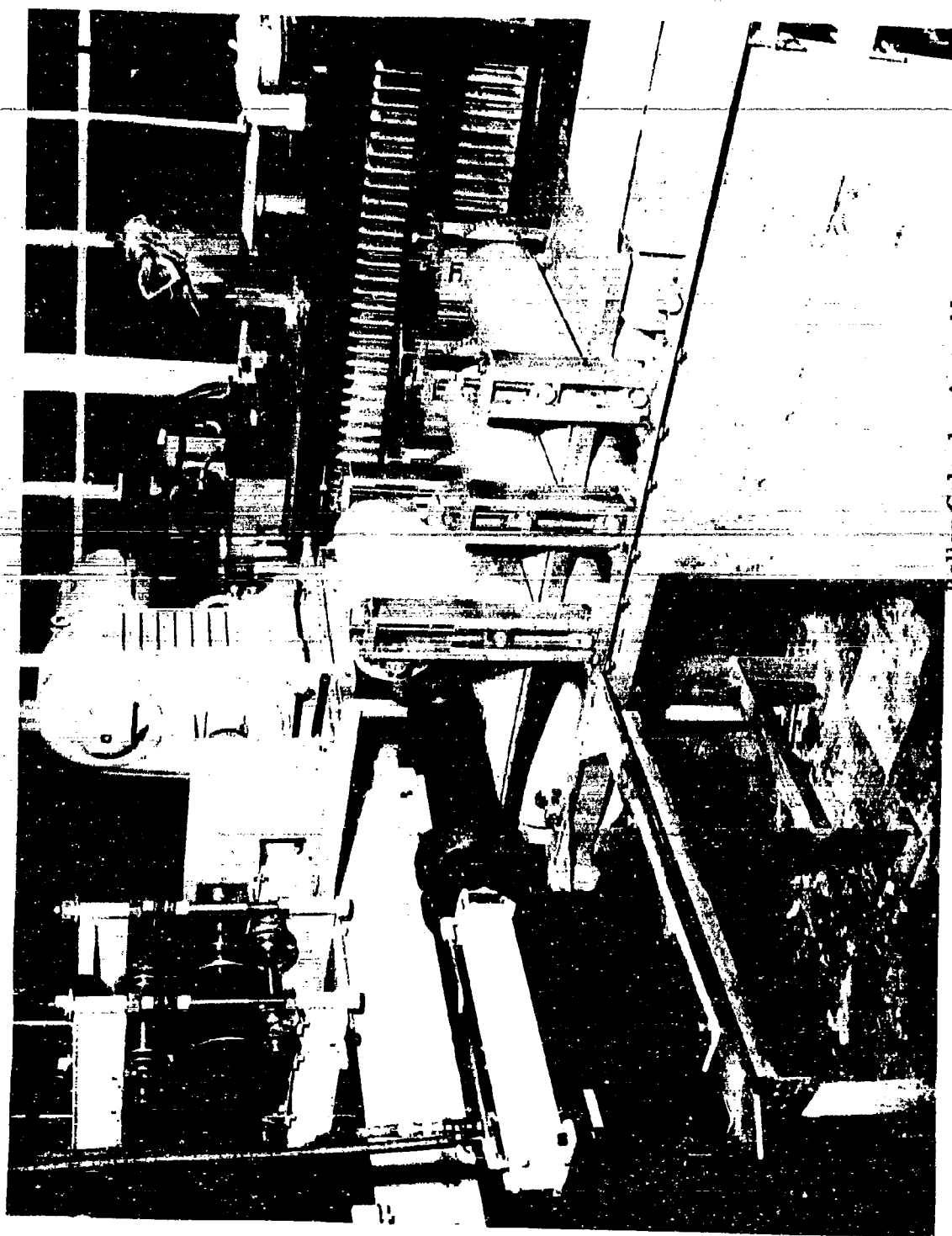
## Test Data:

Run No.	Roll Temp. °F		Roll Speed RPM		Roll Deflection	Comments
	Front	Rear	Front	Rear		
1	105	105	49	30	.100	Dry blend passed with cellophane parting film through nip of rolls - Roll temp. did not melt resin mat'l jogged through to increase heat transfer
2	150	150	49	30	0.050	
3	205	205	20	20	0.150	
4	205	205	jagged rolls		0.150	{ Center of formed sheet not fused-not enough heat transfer-jogging caused rippling of sheet
5	205	205	jagged rolls		0.050	
Preheat dry blend to 150°F in oven then pass through rolls while reducing roll gap from 0.150-0.100						
6	235	235	20	20	0.150 0.100	Good sheet-still needs higher preheat and roll-temperature, lower roll speed

Sketch 3Roller - Calender Assembly

1. Parting Paper Rolls (11.5" wide)
2. Ram Feed Extruder (1/4" x 4" slot die)
3. Glass Flake Ribbon (1/4" x 4")
4. Calendaring Rolls (Adjustable Gap, 13" wide)
5. Conveyor Rolls (13" wide)
6. Conveyor Belt (13" wide)

Photograph 3



Roller Calendar Assembly

Some of the physical test data obtained from the highly oriented 50/50 epoxy-glass laminates produced from calender-rolled B-stage sheet material are presented in Table 20.

Glass flake epoxy resin blend (60/40) were calendered and sheets of the material molded into 3/16" laminates. The flat laminates were free of entrapped air and are highly oriented. The specimens exhibit none of the pearl opalescence associated with mis-orientation or non-wet out flakes.

The 70/30 glass flake epoxy resin blend was calendered into sheets 1/16" and 1/32" thick. The B-stage sheet produced by the 70% blends were not the compacted transparent, uniform sheet obtained from processing lower glass content premixes. The batch did compress but, because of the high glass flake content, once it was past the last roll it became a relatively loose oriented sheet. Apparently, the higher glass content adversely affected the handling characteristics of the B-stage sheet.

To determine if the high quality of the laminates which have been molded could realistically be attributed to the use of the oriented, flat B-stage sheets, the oriented B-stage sheets were divided into equal parts. The flat, oriented B-stage sheets were dielectrically heated for a uniform period of time. The dielectric treatment softened the B-stage resin to produce pliable sheets. One pile of sheets was carefully placed in the mold to ensure that the glass flake orientation was undisturbed prior to mold closure and cure. The 50/50 glass flake-epoxy laminate produced was free of all visual defects such as dis-orientation of flake or air entrapment.

The second group of oriented sheet was rolled into a ball by hand prior to being placed in the mold. The balling of the flat sheets prior to cure produced relatively poorer quality laminates. The laminate was still transparent and free of entrapped air bubbles but many dis-oriented flow lines and pearly opalescent areas denoting mis-orientation were visible.

The results indicate that elimination of turbulent flow during molding through use of oriented B-stage sheets produces laminates which are virtually free of all mechanical defects.

In Table 21, the effect of this processing had upon the glass flake size distribution of the premix and resultant laminates is shown. The data indicates that calender-orientation is a non-flake degrading process and produces visually superior laminates.

#### IV.3.3.2.2.1. Thickness Study

The parting paper may be removed from the roller oriented wet sheets if the sheet material is cooled below 10°F. The cohesive strength of the sheet is increased so that handling during subsequent processing is less difficult. Laminates have been molded containing 7-8 layers of wet non-B-stage sheets processed in this fashion.

**TABLE 20**  
**Properties of Laminates Prepared From Calendered Oriented Sheet Material**

Sample Identification	% Glass Flake	Glass Flake Size	Tensile Str. $\times 10^3$ psi Average	Standard Dev. $\times 10^3$	Tensile Mod. $\times 10^6$ psi Average	Standard Dev. $\times 10^6$	Flexural Str. $\times 10^3$ psi Average	Standard Dev. $\times 10^3$	Flexural Mod. $\times 10^6$ psi Average	Standard Dev. $\times 10^6$	Compressive Str. $\times 10^4$ psi Average	Compressive Mod. $\times 10^5$ psi Average	Thickness
ELR 1-1	50	Uncl.	7.6	n=4 2.6	2.2	n=4 -	18.6	n=7 -	2.5	n=7 -	2.13	3.2	.150
ELR 1-2	50	Uncl.	14.5	n=5 1.1	2.3	n=5 1.1	25.1	2.3	3.3	.25	1.94	3.6	.094
ELR 1-3	50	Uncl.	7.3	n=4 1.3	2.0	n=4 -	17.6	-	2.5	-	2.24	2.6	.150
EL 19-11*	50	Uncl.	9.3		2.8		14.0		2.6		2.55	6.5	.250

Supplement to Table 20

95% Confidence Limits

	95% CL Tensile Str. $\times 10^3$	95% CL Tensile Mod. $\times 10^6$	95% CL Flex. Str. $\times 10^3$	95% CL Flex. Mod. $\times 10^6$
ELR 1-1	11.7 $\leftrightarrow$ 3.5	-	-	-
ELR 1-2	15.9 $\leftrightarrow$ 13.1	2.5 $\leftrightarrow$ 2.1	27.2 $\leftrightarrow$ 23.0	3.5 $\leftrightarrow$ 3.1
ELR 1-3	9.4 $\leftrightarrow$ 5.2	-	-	-



Table 2

**Glass Flake Breakdown Study**  
**Calender - Oriented Sheets**

	<u>% +8</u>	<u>% +16</u>	<u>% +30</u>	<u>% +50</u>	<u>% +100</u>	<u>% Pan</u>	<u>% Loss</u>
Original Glass	52.5	23.5	14.0	7.0	3.0	Trace	0.0
Wet Premix	0.0	1.8	14.9	41.1	27.5	14.4	0.3
Orientated 1st Pass	0.0	0.2	3.2	50.5	27.7	18.0	0.4
Orientated 2nd Pass	0.0	0.2	3.3	49.9	28.1	17.3	1.4
ELR 1-1 (Balled)	0.0	0.0	2.4	50.8	28.9	17.4	0.5
ELR 1-3 (Orientated)	0.0	0.0	12.8	42.7	27.1	16.8	0.6

Wet Premix 50/50

Original Glass - Unclassified Flake

TABLE 22

Molding Parameters for Thick Laminates  
Prepared from Calendered Orientated Sheet Material

Sample Identi- fication	% Glass Flake	Glass Flake Size	"B" Staged	Preheat Time, sec.	P Pressure, lbs.	T <sup>o</sup> Temp., °F.	T Time min.	No. of Laminates	Laminate Thickness in.
ELRX-1	50	Uncl.	Yes	90	2500	250	30	26	2.0
ELRX-2	50	Uncl.	Yes	90	2500	250	30	13	0.951
ELRX-3	60	Uncl.	Yes	70	2500	250	30	14	0.900
ELRX-4	70	Uncl.	Yes	60	2500	250	30	15	1.125
ELRX-5	80	Uncl.	Yes	60	2500	250	30	15	0.827

Regardless of non-uniformity of sheet thickness, the quality (orientation of flake, freedom of visible flaws and entrapped air bubbles, color and lack of opacity or pearl opalescence) of the molded laminates was superior to laminates of equal thickness produced from the loose bulk premix.

Preliminary physical test data obtained from two laminates are presented in Tables 23 and 24. Examination of the preliminary data reveals that a significant increase in tensile strength and compressive modulus have been realized. The increased tensile strength is still below the 25,000 psi value.

#### IV.3.3.2.2.2. Conclusions

Roller calendering has been developed to a high degree of effectiveness, capable of continuously producing oriented compressed glass flake sheet material. The versatility of the technique is sufficient to permit processing a range of sheet thicknesses without effecting glass flake size orientation. The processed sheet may be B-staged prior to lamination although an effective means of laminating wet uncured sheets has been developed.

The visual quality of the laminates produced from wet and B-stage calender oriented sheet materials are noticeably superior to similar laminates processed through other mechanisms or techniques.

Indications have been obtained that this process could be an effective means of producing molding materials capable of molding complex shapes such as radomes, rocket exhaust nozzles and practice nose cones and a wide variety of products requiring superior dielectric properties which would be free of most of the flake disorientation and flow line problems now encountered in most glass flake molding.

Optimization of the calendering technique requires that the reduction of nip calender roll clearance between successive pairs of rollers be gradual. Therefore, to increase the effectiveness and efficiency of the assembly the number of pairs of calendering rolls should be increased to permit this gradual reduction in nip clearance. An assembly with ten pairs of rolls is presently believed to be adequate. The first two pairs of rolls would be corrugated-metering rolls permitting the direct addition of non-oriented flake from the mixer onto the conveyor.

The rate of decrease in nip clearance is critical. The glass flake resin system as it passes through the nip roll is compressed. If the nip clearance is decreased more than  $1/16"$ , a heavy resin-flake bead or wave forms on the feed side of the roll. The effect of the bead is two-fold: (1) the turbulence in the bead causes breakdown in glass flake particle size and (2) it increases drag on the roller assembly.

TABLE 23  
Physical Properties of Oriented Laminates

Sample Identi- fication	% Glass	Glass Flake Size	Thickness in.	Compressive Strength psi <sub>3</sub> x10 <sup>3</sup>	Compressive Modulus psi <sub>6</sub> x10 <sup>6</sup>	Tensile Strength psi <sub>3</sub> x10 <sup>3</sup>	Tensile Modulus psi <sub>6</sub> x10 <sup>6</sup>	Flexural Strength psi <sub>3</sub> x10 <sup>3</sup>	Flexural Modulus psi <sub>6</sub> x10 <sup>6</sup>
ELR-2-5	70		0.105±.003	22.2	2.23	6.0	3.2	13.7	3.2
ELR-2-5	70		0.165±.003	21.0	2.13	8.2	2.8	23.2	4.36
EL-19-16	70		0.250	13.6	0.84	2.9	2.0	12.1	3.4
EL-19-18	70		1.0	24.7	0.80	4.8	-	13.3	4.5

TABLE 24  
Physical Properties of Oriented Laminates

Sample Identification	Glass Flake %	Tensile		Flexural		Standard 6		Compressive		Standard 6		Laminate Thickness in.
		Strength $\times 10^3$ psi	Modulus $\times 10^6$ psi	Strength $\times 10^3$ psi	Modulus $\times 10^6$ psi	Strength $\times 10^3$ psi	Modulus $\times 10^6$ psi	Strength $\times 10^3$ psi	Modulus $\times 10^6$ psi	Strength $\times 10^3$ psi	Modulus $\times 10^6$ psi	
		Avg.	n = 3	Avg.	n = 3	Avg.	n = 4	Avg.	n = 5	Avg.	n = 5	
ELR 2-1	60	11.7	3.5	23.6	0.7	5.2	0.8	27.6	6.1	2.5	1.0	0.085
ELP 2-2	60	11.9	2.8	24.8	1.6	3.6	0.3	27.8	2.9	3.0	0.8	0.180
ELR 2-3	60	12.5	3.1	15.6	-	3.5	-	22.1	3.5	2.1	0.4	9.165
ELR 2-4	60	8.2	2.4	26.1	-	3.3	-	25.8	2.9	2.2	0.4	9.170
ELR 2-5	70	5.9	3.2	13.6	-	3.2	-	22.2	2.6	2.2	0.6	0.105
ELR 2-6	70	unc1.	2.8	29.1	6.7	4.4	0.6	21.2	3.1	2.1	0.5	0.165
ELR 2-10	50	8.3	1.3	24.3	1.8	2.8	0.2	29.7	6.6	2.4	0.6	0.275
ELR 2-11	50	10.6	3.1	21.9	-	4.5	-	27.0	1.5	2.1	0.1	0.110
ELR 3-2	60	9.4	3.6	23.9	-	4.7	-	22.3	4.8	1.8	0.8	0.140
ELR 3-3	60	7.2	1.5	18.9	2.6	3.6	0.2	25.6	2.3	2.3	0.4	0.210
ELR 3-4	60	10.4	2.8	57.5	-	8.8	-	25.0	4.0	2.0	0.4	0.145
SL 3-11	70	2.0	-	4.7	0.4	1.6	0.06	5.3	1.2	0.6	-	0.213

Effect of Calendar-Oriented Process on Physical Properties

Sample Identification	% Glass Flake	Calendar Oriented	Thickness in.	Tensile		Flexural		Compressive	
				Strength $\times 10^3$ psi	Modulus $\times 10^6$ psi	Strength $\times 10^3$ psi	Modulus $\times 10^6$ psi	Strength $\times 10^3$ psi	Modulus $\times 10^6$ psi
				Avg.	Avg.	Avg.	Avg.	Avg.	Avg.
ELR 2-10	50	+8	0.275	8.3	1.3	24.3	2.8	29.7	2.4
ELR 2-11	50	+8	0.110	10.6	3.1	21.9	4.5	27.0	2.1
EL 18-11	50	unc1.	0.250	9.3	2.8	14.0	2.6	25.5	0.65
ELR 2-5	70	unc1.	0.105	5.9	3.2	13.6	3.2	22.2	2.2
ELR 2-6	70	unc1.	0.165	8.2	2.8	28.1	4.4	31.0	2.1
EL 19-16	70	unc1.	0.250	2.9	2.0	12.1	3.4	23.6	0.84
EL 19-18	70	unc1.	1.0	4.6	-	13.3	4.5	24.7	0.80
ELR 2-1	60	+8	0.085	11.7	3.5	23.6	5.2	27.6	2.5
ELR 3-4	60	+8	0.145	10.4	2.8	57.5	8.8	25.0	2.0
ELR 3-3	60	+8	0.210	7.2	1.5	18.9	3.6	25.6	2.3

Supplement to Table 24

95% Confidence Limits

	<u>95% CL</u> <u>Flex. Str. x 10<sup>3</sup></u>	<u>95% CL</u> <u>Flex. Mod. x 10<sup>6</sup></u>	<u>95% CL</u> <u>Comp. Str. x 10<sup>3</sup></u>	<u>95% CL</u> <u>Comp. Mod. x 10<sup>6</sup></u>
ELR 2-1	24.7 ↔ 22.5	6.5 ↔ 3.9	35.2 ↔ 20.0	3.7 ↔ 1.3
ELR 2-2	27.3 ↔ 22.3	4.1 ↔ 3.1	31.4 ↔ 24.2	4.0 ↔ 2.0
ELR 2-3	-	-	26.6 ↔ 17.6	2.6 ↔ 1.6
ELR 2-4	-	-	29.4 ↔ 22.2	2.7 ↔ 1.7
ELR 2-5	-	-	25.4 ↔ 19.0	2.9 ↔ 1.5
ELR 2-6	38.8 ↔ 17.4	5.4 ↔ 3.4	25.0 ↔ 17.4	2.7 ↔ 1.5
ELR 2-10	27.2 ↔ 21.4	3.1 ↔ 2.5	37.9 ↔ 21.5	3.1 ↔ 1.7
ELR 2-11	-	-	28.9 ↔ 25.1	2.2 ↔ 2.0
ELR 3-2	-	-	28.3 ↔ 16.3	2.8 ↔ 0.8
ELR 3-3	23.0 ↔ 14.8	3.9 ↔ 3.3	27.2 ↔ 24.0	2.8 ↔ 1.8
ELR 3-4	-	-	29.9 ↔ 20.1	2.5 ↔ 1.5
SL 3-11	5.4 ↔ 4.0	1.7 ↔ 1.5	6.8 ↔ 3.8	-

The processing of all these systems was accomplished with no difficulty. Control of roller nip clearance and redesign of some of the components of the assembly have eliminated many of the mechanical problems previously reported.

#### IV.3.3.3. Dielectric Preheating

Dielectric preheating has shown unusual usefulness for preheating of many industrial thermosetting compounds. The use of dielectric preheating has made the technique of transfer molding thermosetting compounds feasible. It has been speculated that the use of dielectric preheating of glass flake premixes would result in cured laminates with greater uniformity of physical characteristics. Heat transfer properties and temperature gradients throughout the part being molded differ widely when thick sections are molded. This results in a cured piece that has mechanical properties that may vary with the part thickness, i.e., the center may be undercured and be very weak, while the outer edge, having been cured normally, would exhibit predicted properties.

The Futuramic Molded Products, Hartford, Connecticut, cooperated in permitting a few preliminary tests and a brief study of the usefulness of a dielectric heater at their facilities. Since the production plant was not equipped with test facilities, the results were obtained by observation and pot temperature readings.

The epoxy dry blend containing 70% glass flake was uniformly heated to 170°F. and 250°F. in 20 and 60 seconds respectively (Table 25). A temperature of 300°F. was reached in 150 seconds with local overheating, as indicated by scorching. After heating for 20 seconds, the premix was tacky and could be compressed readily to a bulk volume about twice the final molded volume. After heating for 60 seconds, the blend could be further compressed, but the cure seemed to be advanced too far to allow any time for process handling or making satisfactory preforms (Table 26).

The dielectric heater settings for the dry blend, heated the wet blends too rapidly, and the temperatures attained were above 300°F. with localized scorching. The high resin content became heated at a higher rate than did the lower resin content mixes, as illustrated in Figure 5. To retard the heating rate, an aluminum spacer was placed between the 70% glass premix and the electrode of the unit. This technique proved effective in controlling the heating rate.

These few preliminary tests established preheating parameters and showed that dielectric heating is feasible and desirable for making usable preforms from dry blends and heating thick sheets of wet mix to a uniform curing temperature before applying pressure in a heated press.

TABLE 24  
SUMMARY OF PREPARE AND MIXING PARAMETERS FOR  
DRY BLENDS OF EPOXY-AMINE AND EPOXY RESIN SYSTEMS

Laminate Identification	Preforming Parameters		No. of Preforms	Molding Parameters				Comments	% Glass	Sheet Appearance	Resin Type	Resin Formulation Typical Wt.	Resin Preparation & Mixing	Glass Size
	Pt	Pa		Cr	Co	Mo	Ma							
EL-15-18	220	90	C	2	220	1.5	220-370	45	30	Wrinkled edges	C	JD 510 MPD	100 14	
-19	170	15	250	2	220	1.5	220-370	45	30	Buckled mold plate - Not tested-Warped Sheet	B	Epoxy Amine Cured		
-20	170	15	250	2	220	1.5	220-370	45	20	Slightly cloudy	B			
-21	170	30	250	1	220	1.5	220-370	45	15	Clear Sheet	B-A			
-22	170	30	250	2	220	1.5	220-370	45	30	Good	A			
-23	170	30	250	1	220	1.5	220-370	45	30	Good	A			
-24	160	15	200	1	170	0	170	45	20	Clear center-dry edges - Not tested	D	JD 510 MPD	100 14	
-25	160	30	200	1	220	0	220	45	30	Poor Resin flow-not tested	C	Epoxy Amine Cured		
-26	160	20	200	1	350	0	350	10	20	Improperly molded - Not tested	C			
-27	160	20	200	0	0	0	370	45	30	Clear-Some Exotherm spots	B-C	"	1	
-28	160	20	200	0	0	0	320	45	30	Good sheet	B			
-29	160	20	200	0	0	0	270	45	30	Good sheet	A			
-30	160	20	200	1	240	0	240	45	30	Dry Corners	B			
-31	160	20	200	1	270	1.5	270	35	30	Good, sl. wrinkles in corners	B	"	1	
-32A	160	20	200	3	270	2	270	35	30	Good, sl. wrinkles in corners	A			
-32B	160	20	200	0	0	0	270	35	30	Good, sl. wrinkles in corners	A			
-33	160	30	200	1	270	0	270	35	30	Poor edges - Not tested	C	JD 510 MPD	100 14	
-34	160	30	200	2	270	1.5	270	35	30	Fair appearance	B			
-35	160	30	200	2	270	2.5	270	35	30	Poor - not tested	C-D			
-36	160	30	200	2	270	2.5	270	35	30	Poor - not tested	C-D			
-37	160	30	200	2	240	0	240	2 hr 30	30	Excellent sheet	A	"	1	
-38	160	30	200	2	370	0	370	2 hr 30	30	Excellent sheet	A	"	1	
EL-25-1	-	-	-	0	350	0	350	45	30	Variegated Appearance	B-C	JD 560 JD 509 MPD	60 40 6.7	U
EL-26-1	170	20	200	2	300	0	300	2 hr 30	30	Excellent sheet	A	JD 522 MPL	100 1.9	U
EL-26-2	170	20	200	2	300	0	300	2 hr 30	30	Excellent sheet	A			



TABLE 2  
SUMMARY OF PREFORMING AND MOLDING PARAMETERS FOR  
DRY BLENDS OF AUSTINITE AND EPOXY RESIN SYSTEMS

Laminate Identification	Preforming Parameters			No. of Preforms	Molding Parameters				Comments	% Glass	Sheet Appearance	Resin Type	Resin Formulation Typical Wt.	Resin Preparation & Mixing	Glass Size
	Pt	Fa	Pp		Cg	Mp	Kp	Kp							
EL-15-16	220	90	C	2	220	1.5	220-370	45	30	Wrinkled edges	70	C	JD 510 MPD 14		
-19	170	15	250	2	220	1.5	220-370	45	30	Buckled mold plate - Not tested/Warped Sheet	50	B	Epoxy Amine Cured		
-20	170	15	250	2	220	1.5	220-370	45	20	Slightly cloudy	50	B			
-21	170	30	250	1	220	1.5	220-370	45	15	Clear Sheet	50	B-A			
-22	170	30	250	2	220	1.5	220-370	45	30	Good	60	A			
-23	170	30	250	1	220	1.5	220-370	45	30	Good	60	A			
-24	160	15	200	1	170	0	170	45	30	Clear center-div edges - Not tested	80	D	JD 510 MPD 14		
-25	160	30	200	1	220	0	220	45	20	Poor Resin flow - not tested	80	C			
-26	170	-	200	1	350	0	350	10	30	Improperly molded - Not tested	80	C	Epoxy Amine Cured		
-27	170	20	200	0	-	0	370	45	10		70	B-C			
-28	170	20	200	0	-	0	320	45	30	Clear-Some Brothens Spots	70	B	"	1	
-29	160	20	200	0	-	0	270	45	30	Good sheet	70	A			
-30	160	20	200	1	240	0	240	45	30		70	B			
-31	160	20	200	1	270	1.5	270	35	30	Dry Corners	70	B			
-32A	160	20	200	3	270	2	270	35	30	Good, sl. wrinkles in corners	70	A	"	1	
-32B	160	20	200							325 post-cured 2 hrs. @ 350°F					
-33	160	30	200	1	270	0	270	35	30	Poor edges. Not tested	80	C	JD 510 MPD 14	1	
-34	160	30	200	2	270	1.5	270	35	30	Fair appearance	80	B			
-35	160	30	200	2	270	2.5	270	35	30	Poor - not tested	80	C-D			
-36	160	30	200	2	270	2.5	270	35	30	Poor - not tested	80	C-D			
-37	160	30	200	2	240	0	240	2 hr 30		Excellent sheet	70	A	"	1	
-38	160	30	200	2	370	0	370	30		Excellent sheet	70	A	"	1	
EL-25-1	-	-	-	0	350	0	350	45	30	Variiegated appearance	70	B-C	JD 560 JD 508 MPD 6.7	2	
EL-26-1	170	20	200	2	300	0	300	2 hr 30		Excellent sheet	70	A	JD 522 MPD 3.9	3	
EL-26-2	170	20	200	2	300	0	300	2 hr 30		Excellent sheet	70	A			

Figure 5

Temperature of Glass Flake-Epoxy Samples  
vs. Exposure Time in Dielectric Heater

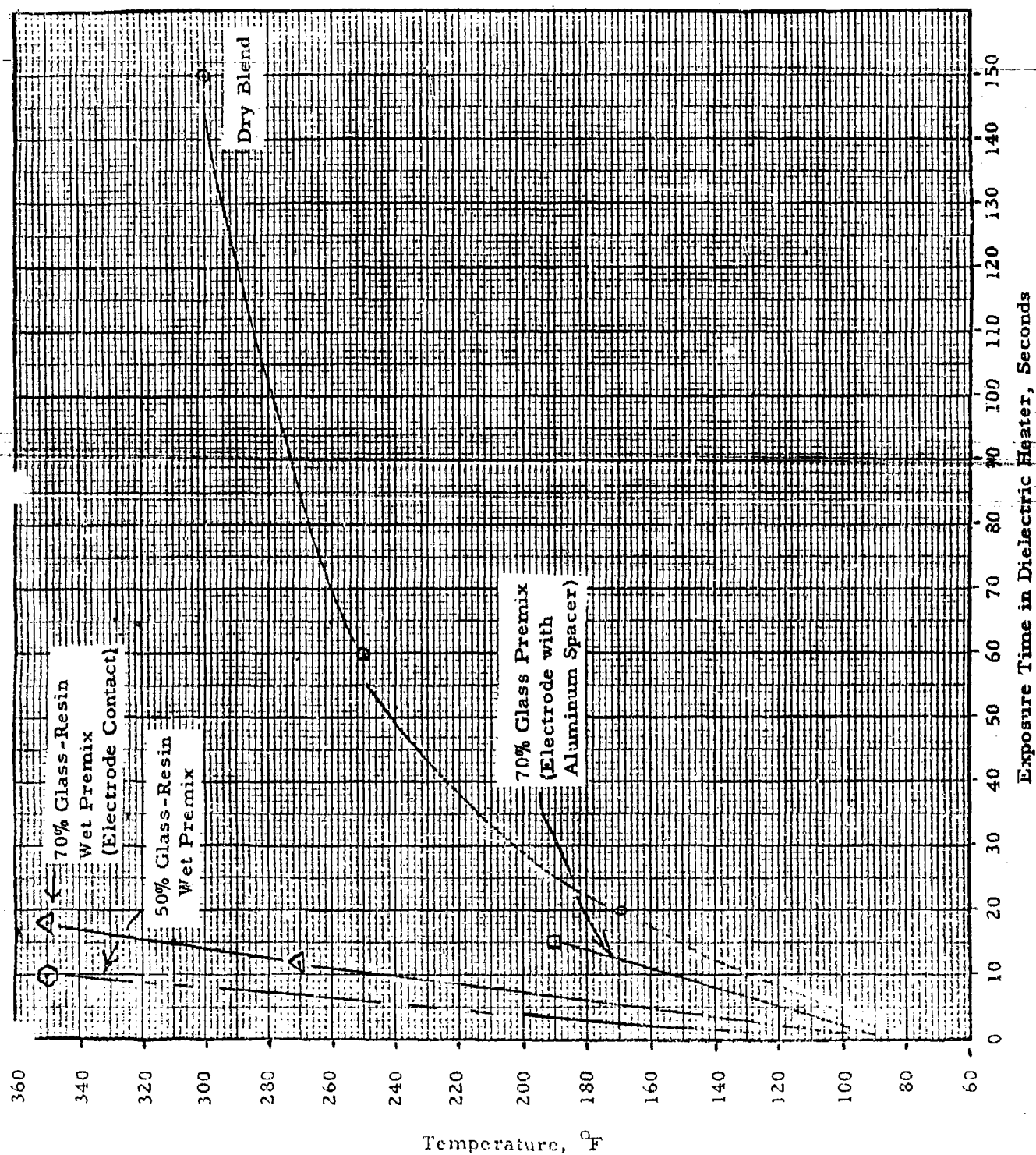


TABLE 26  
SUMMARY OF RECOMMENDED MOLDING PARAMETERS FOR EL-15 SERIES

<u>Preforming</u>			<u>Molding Cycle</u>				
$P_T$	$P_\theta$	$P_P$	$C_T$	$C_\theta$	$M_T$	$M_\theta$	$M_P$
160-170	15-30	200-250	240-370	0-2	240-370	2	30

Key:

$P_T$  = Preforming temperature, °F.

$P_\theta$  = Preforming time, seconds

$P_P$  = Preforming pressure, psi

$C_\theta$  = Time in which preformed dry blend is allowed to come to molding temperature at contact pressure, subsequently referred to as contact time, minutes.

$C_T$  = Contact temperature

$M_T$  = Molding temperature, °F.

$M_\theta$  = Molding time, hrs.

$M_P$  = Molding pressure on 4 1/2 inch ram, tons

#### IV.3.3.3.1. Conclusions

The dielectric heater (Photograph 4) was used throughout the later portion of the program and was found to be a very effective process tool. The heating of premix charges and oriented sheets in the dielectric heater has proved to be vastly superior to relying upon mold dwell time to preheat the laminates. The laminates are effective insulators and do not conduct heat readily. Therefore, dwell time preheating often results in premature and local resin cure. This problem is eliminated through proper use of the dielectric preheater.

#### IV.3.3.4. Extrusion

The purpose of this phase of the program was to determine the feasibility of using extruders to process preformed glass flake shapes. Cure of the preforms could be accomplished at the time of extrusion or in a later process step.

The advantages of such a process would be continuous production of an intricate shaped profile which is a finished or semi-finished product. If delayed cure of the shape were possible, cure after insulation and even resin bonding to the total component may have been possible.

The process was to be evaluated using a spiral screw extruder and a ram extruder (injection molder). The use of two extruder systems would permit comparison of the degradation effects of the process upon the glass flake premix.

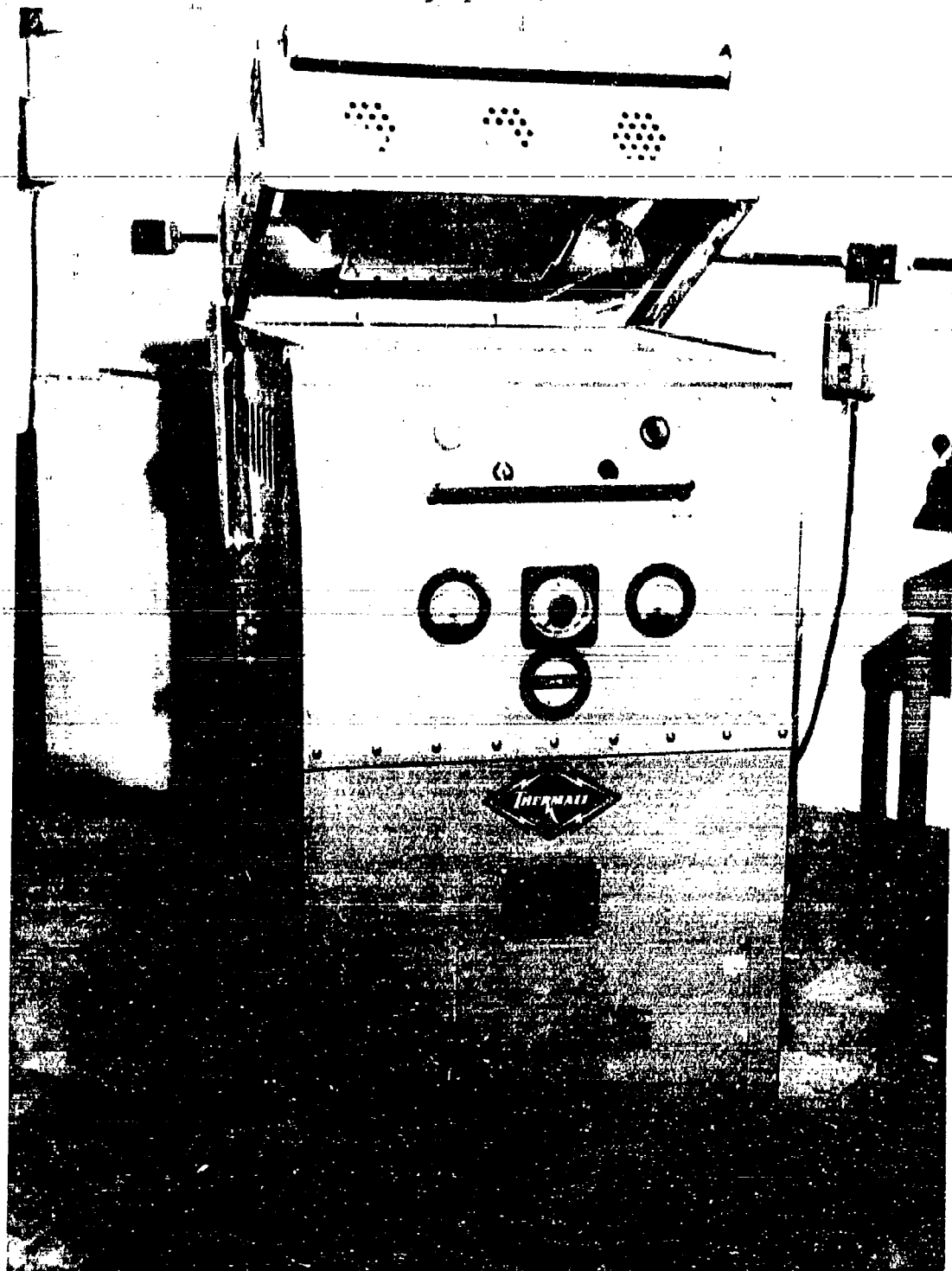
The extruders were to be used with premixed systems and not as methods of blending flakes with resin binders.

Investigation of the applicability of extrusion of glass flake premixes with thermosetting binders was evaluated with the two separate development trials.

Approximately 2000 grams of a 50% glass flake-polyester resin premix was prepared in the Abbe mixer for three test runs in the 1-1/2" MPM extruder. Photograph 5 shows the equipment used. (In the picture is a pipe die and the 3:1 compression ratio used screw during the study.) The polyester premix used consisted of Laminac 4128 (American Cyanamid) and benzoyl peroxide, 1% (Cadet Chemical Company). This premix was extruded in the following shapes:

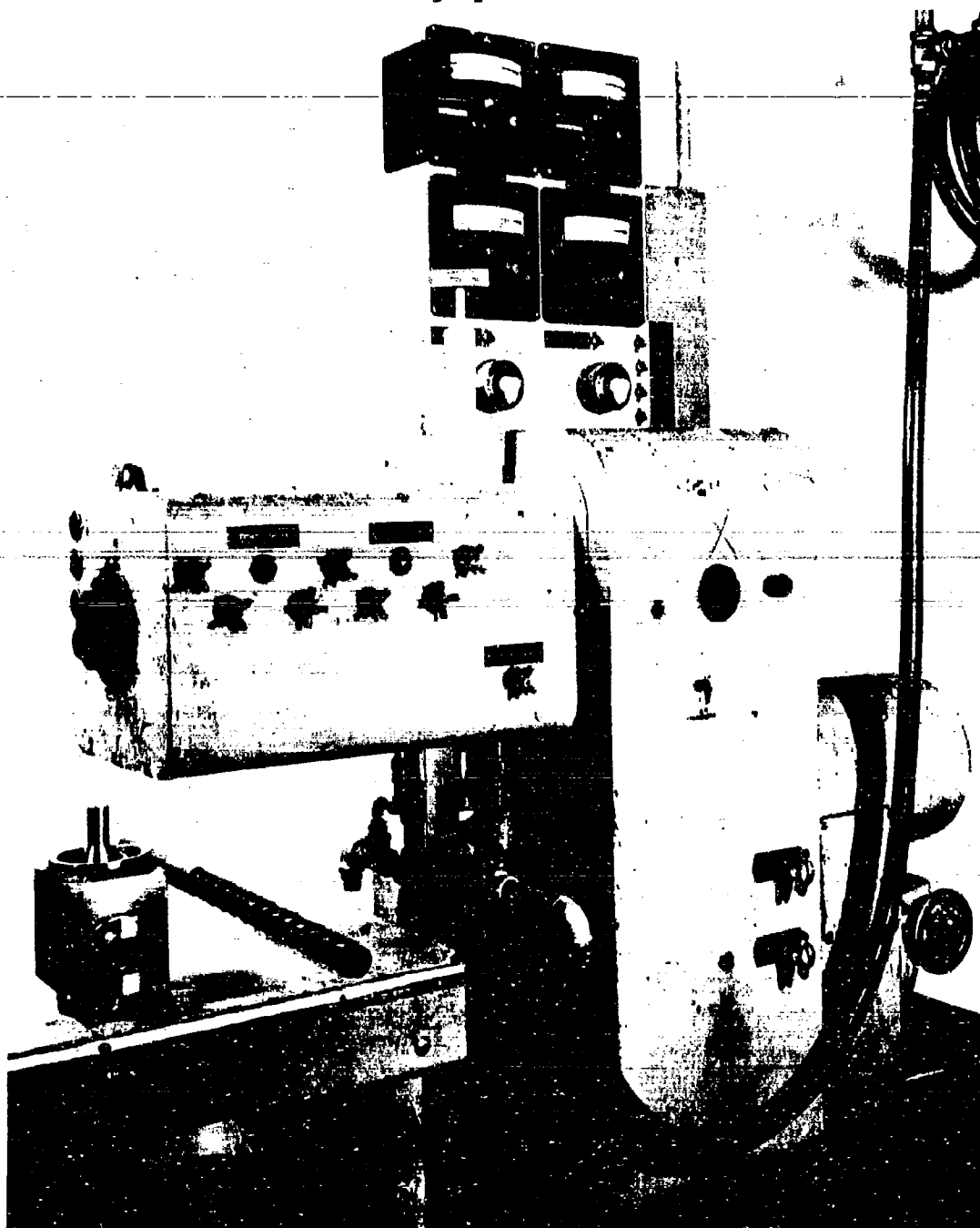
- (a) Sheet - a 3 inch adjustable thickness, right angle die was used. Sheet could not be extruded continuously at any thickness from 0.016 to 0.040 and at four screw speeds, the difficulty being that the extrudate would not cohere, and also that the material extruded intermittently from various sections of the 3 inch slit.

Photograph 4



Thermall Dielectric Heater

Photograph 5



One and One-half Inch MPM Extruder  
With Pipe Die and 3:1 Compression  
Ratio Extruder Screw

- (b) Hollow Pipe - a one-inch diameter right angled pipe die with mandrel was used to attempt to extrude a hollow pipe continuously. The same difficulties experienced with extrusion of sheet were also encountered here; the extrudate was not self-supporting.
- (c) Solid Rod - a 3/16 inch diameter rod die was then installed on the extruder. Extrusion of this solid shape was more successful than the other shapes investigated. A continuous rod was extruded for a short period. (Extrusion was too erratic to obtain rates.) Screw speeds of 13 rpm, 39 rpm, and 78 rpm were used. The extruded rod had a fluffy appearance because of low die pressures, bridging of the premix in the metering zone of the extruder screw, and poor cohesion.

The attempt to extrude a polyester glass flake premix through a sheet film die, a tubing die, and a rod die, was unsuccessful because of poor cohesion of the glass flake premix after extrusion. It was postulated that the use of a smaller glass flake size in the premix would aid in the obtainment of a better extruded shape. Additionally, low die pressures were believed responsible for poor compacting of the premix during the former trial. An extruder screw with a higher compression (5:1) ratio was obtained and a device to force feed the first feed zone of the extruder was fabricated and installed. (An extruder screw with a low compression ratio of 3:1 was used for the first trial; premix feeding difficulties had been encountered at this time.)

For this study, a premix\* containing 50% of -16 mesh glass flake with an epoxy binder was extruded through the 3/16 inch diameter rod die which had shown the most promise during the last run.

The premix was extruded continuously at ambient temperatures, at rates of 2.3 and 52 pounds per hour. At both the high and low rates, the extrudate had poor self-cohesion. At the 2.3 lb./hr. rate, unhomogeneous extrusion of the premix was observed, while extrudate uniformity at the 52 lb./hr. rate appeared excellent. The force feed mechanism operated satisfactorily assuring constant feed to the feed zone of the extruder screw. The extrusion operation was carried out at ambient temperatures to prevent polymerization of the thermosetting premix within the extruder barrel. Although the rod die used was equipped with heaters, these were not used since a one hour retention at the curing temperature would have been necessary to induce polymerization of the premix to render it solid.

Table 27 presents operating data for this run.

Photograph 6 illustrates the appearance of the glass flake mix as it is extruded through the rod die. Photograph 7 shows cured extrudate yields from the 3/16 inch diameter rod die.

\* Refer to Table 27 for formulation.

TABLE 27  
DATA TAKEN FOR EXTRUSION OF EPOXY-GLASS FLAKE PREMIX

Run No.	T <sub>screw</sub>	T <sub>liner</sub> Zone 1   2   3			Die Temp. of.	RPM Screw	Die Type	Flow LBS./HR.	CR Screw	Extrudate Quality
1	Ambient	Ambient			Ambient	26	3/16" DIA Red Die	2.3	5:1	Poor Cohesion Intermittent Extrusion of Resin Rich Premix
2						100		52.0	5:1	Better Appearance Same Poor Cohesion of Extrudate

T<sub>s</sub> = Extruder Screw Temperature, °F

CR Screw = Compression Ratio of Extruder Screw

Equipment:

1 1/2 inch RPM Extruder  
L/D Ratio = 14:1

Premix Composition: (By Weight)

30% Resin (Jones Dalney (Epoxy) 509 100 Parts, Methyl Methac Anhydride 90 Parts, DMP-10 2 Parts)  
70% -16 Mesh, 2 Micron Glass Flake

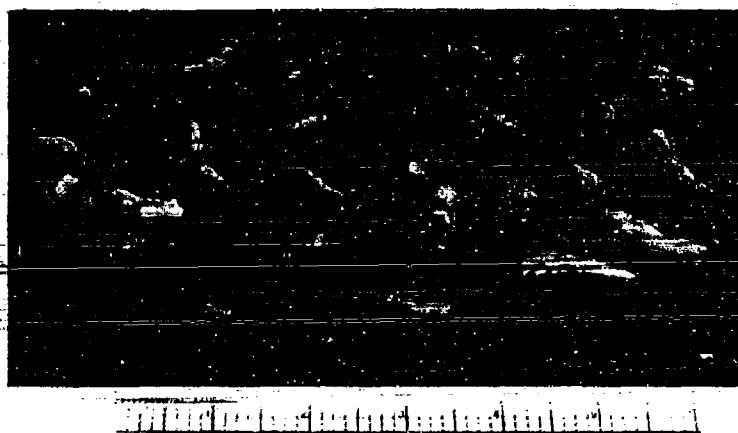


Photograph 6



Extrudate Appearance  
During Extrusion

Photograph 7



Extrudate Appearance After  
Extrusion and Curing

To determine the applicability of injection molding glass flake reinforced plastics, a Van Dorn injection molding machine pictured in Photograph 8 was modified for developmental tests. The Van Dorn injection molder is designed for the rapid molding of thermoplastic resins. Inasmuch as thermosetting resins were being used as binders, the following modifications were made:

All the band heaters which preheat the molding compound in the preheat barrel prior to injection into the heated mold were disconnected. This action was taken to prevent polymerization of the thermosetting resin system within the barrel. The die only, as ASTM standard tensile bar configuration, was heated. The clamping head which houses the sprue and sprue bushing was not heated in order to prevent conduction of heat to the injection nozzle.

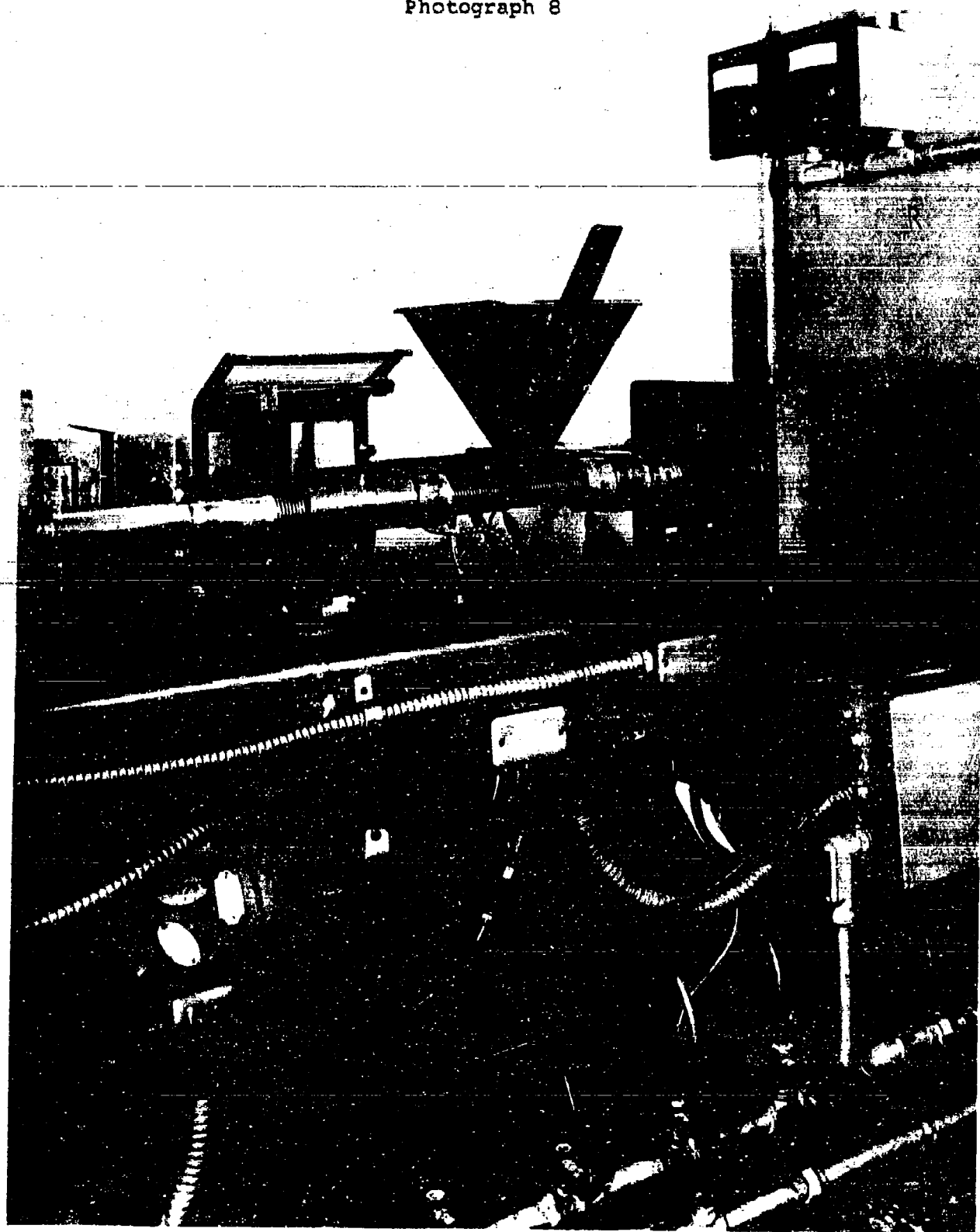
A premix containing 50% glass flake and 50% Laminac 4128 (American Cyanamid) polyester resin catalyzed with 2% benzoyl peroxide was used for the trials.

The factors of short cure time and long pot life were the basis for choosing this resin system over any epoxy, phenolic, or silicone resin binder.

The normal cycling of this injection molding machine is as follows: pelletized thermoplastic resin is stored in a chamber to the rear and above the preheat barrel. At a preset cycle time, the injection ram withdraws beyond the bottom of the feed hopper and so allows a certain volume of thermoplastic to enter the heating barrel. During the remainder of the cycle, the resin is advanced by the intermittent plunger action through the heating barrel and rendered molten. At the last stage of the cycle, the two heated die faces are clamped together under pressure and the ram injects a fixed charge of molten resin through the sprue bushing into the die which is at a lower temperature than the preheat barrel. The molten resin then "freezes" in the die and is automatically ejected from the die. Production capacity of this machine ranges from 20-60 molded parts per hour depending upon the resin used and the molded weight of each part.

During the trial run, difficulties were encountered in the feeding of the premix in the barrel of the machine. The material continually bridged and had to be forced into the barrel cavity by hand. After the barrel of the unit had been filled with premix, it was injected into the clamped tensile bar mold and cured for a period of 10 minutes. When the die was opened, it was observed that the fill of the tensile bar cavity by the premix was insufficient. Additionally, the premix had cured in the sprue and sprue bushing even though the sprue bushing was not heated. The exothermic curing of the premix in the die had evidently propagated curing in the injection nozzle of the machine. (Ordinarily, with a thermoplastic resin, the filled sprue cavity is ejected with the finished part.) In this case, several hours were required to disassemble and remove hardened laminate from the sprue bushing. Table 28 presents operating data for the trial run.

Photograph 8



Van Dorn Injection Molding Machine

Table 28Injection Molding Conditions for 50% Polyester-Glass Flake Premix

Mold Temperature Rear Cavity	Temperature Sprue Cavity	Barrel Front	Temperature Rear	Ram Pressure	Cure Time
210°F	Ambient	Ambient		1000psi	10 minutes

Equipment:

2 oz. Van Dorn Injection Molder - Model H 200

In consideration of the operating difficulties experienced, it was concluded that injection molding machines are probably incompatible with thermosetting plastics requiring lengthy curing times. Work was discontinued on this phase.

#### IV.3.3.4.1. Conclusions

The extruder runs performed demonstrated that this method of fabrication at glass contents used was not feasible. The polyester and the epoxy binders used typify the handling characteristics encountered with premixes made from any of the four resin systems under study. Poor cohesion of the extrudate when formed into sheet, hollow rods, tensile bars, or solid rod shapes has been the principal problem. Long thermoset resin cure compared with the normal thermoplastic rapid cooling-hardening properties also presents major problems.

In essence, complete machine redesign would be necessary to extrude thermosetting compounds. For these reasons, it is concluded that the process of extrusion of thermosetting glass filled compounds is not amenable using standard thermoplastic extruding machines. Development work on the extrusion phase was discontinued as a result of these poor results. This abandonment permitted additional emphasis on process development for techniques having greater potential in parts manufacture.

#### IV.3.4. Molding Techniques

The work described in this section encompasses the experimental and pilot plant development of the use of glass flake-resin mixtures in conventional plastic processes. Screening experiments with compression molding, rotational molding, centrifugal casting and extrusion are reported. As a result of these studies, extensive pilot plant effort was expended in developing useful compression molding and centrifugal casting processes. The developments coupled with our success in devising intermediate steps of mixing and flake orientation led to the preparation of high quality laminates.

##### IV.3.4.1. Compression Molding

The bulk of the laminates described in this report were produced by various compression molding processes. All but two of the complex molded items reported in Phase III were also compression molded. Compression molding consists essentially of placing premix into an open heated mold cavity, closing the mold and applying pressure to the premix causing orientations, compression and cure of the system.

##### IV.3.4.1.1. Thickness Study

The objective of this phase was to study the molding characteristics and the mechanical properties of simple flat slabs compression molded from glass flake reinforced premixes using either epoxy, polyester, phenolic, and silicone resins as binders. Thicknesses of the slabs ranged from 1/16 inch to 2 inches, (Photograph 9). Two glass contents, 50% and 70%, were used in the premixes.



Photograph 9

Two Inch Thickness Compression Moldings  
of Glass Flake Reinforced Polyester and Epoxy Resins  
(L.) 50% Glass Flake-Polyester Laminates (7x7)  
(R.) 70% Glass Flake-Epoxy Laminates (7x7)

This study was performed with non-oriented preformed materials. A similar study, using roller calendered sheets having nearly completely oriented flake was performed late in the program.

The reasons for this study are several fold: (1) there are no published data relating to the molding of glass flake reinforced plates thicker than 3/4 inch. (2) The mechanical strengths of varied thickness moldings would have to be determined for ultimate design use. (3) An objective of the program is to determine whether thick pieces could be produced. Many industrial plastics cannot be produced in sections thicker than one inch because of loss of physical properties from exothermic overheating and stress cracking during or immediately after molding.

A standardized mixing technique was used to prepare glass flake premixes for the four resin systems evaluated except as noted later in the text. A preweighed charge of resin and catalyst were mixed in a five-gallon Abbe blender until homogeneous (about 1/2 hour). The glass flake, in the appropriate weight to provide a 50% or 70% (weight) glass content, was added slowly to the fluid resin in the Abbe blender. Mixing was continued at a 40 rpm blade speed for a period of 30 minutes. The mixed batch was discharged and prepared for the compression molding operation either preforming of the premix into thin sheets followed by B-staging or charging the bulk premix directly into the heated mold. The latter technique was used for premixes in which the resin binder could not be B-staged (polyester, silicone).

The epoxy resin formulation consisted of a 75/25 mixture of Devco & Reynolds-Jones Dabney Epi Rez 510 or 509 and 504 cured with Shell Curing Agent 2, a eutectic blend of amines. The 50% glass premix was prepared in the 5-gallon Abbe mixer under a 1 mm. Hg (absolute pressure). After mixing, the premix was discharged into a flat 1/8 inch thick sheet and allowed to cure at room temperature overnight to the B-stage. The sheet was then broken into smaller pieces and charged onto a Cumberland granulator with a 1/2 inch punched plate discharge screen. The granulated material had the appearance of a dry, general purpose molding powder, which was subsequently charged into the preheated 7 x 7 mold. (As learned shortly afterward, this material could be dielectrically preformed and preheated prior to molding using a procedure standard for many other reinforced molding compounds.) The 70% glass epoxy premix was molded directly in the 7 x 7 mold without B-staging.

The same mixing technique described above was used for the polyester system except that the vacuum employed was reduced to 20 mm. Hg absolute pressure (to prevent "boiling" off of the higher vapor pressure components of the polyester resin system.)

Since polyester resins under investigation cannot be B-staged to a hard material capable of being reheated and cured as can the epoxy resin system, the resin wet premix was molded after discharge from the Abbe mixer. The required amount of glass flake reinforced premix was charged into the preheated mold and molded at the pre-determined curing cycle. The polyester glass flake premixes have been consistently more difficult to mold because of high resin drain-off and have also given repeatedly poor tensile properties



in laminates as compared with epoxy laminates.

A solution of phenolic resin, Union Carbide B622600, was used to coat glass flakes in the Hobbs blender. No vacuum was applied during mixing to prevent solvent losses. Subsequent solvent removal from the premix by air circulating ovens and dielectric prebaking did not completely remove residual traces of solvent. The resulting molded parts of the premixes exhibited blistering and delamination. Emphasis was redirected to the use of dry blending techniques to prepare blister-free phenolic glass flake laminates.

Glass flake was added to a Patterson-Kelley V blender and tumbled for a period of one hour prior to addition of the resin to develop a static charge. A pulverized phenolic resin, Resinox RI 4009 (Monsanto Chemical Company), was then added. A two-hour dry blending time was used.

The dry blended phenolic glass flake premixes which were prepared were loose, fluffy, and friable. To permit molding, the loose non-oriented mass was preformed into flat wafers. The wafers were prepared in a 9" x 9" box mold at the preforming conditions of 170°F., under 200 psi pressure for 20 to 30 seconds.

Wafers approximately 1/8" thick were obtained when the 3" deep cavity of the 9" x 9" box mold were filled to capacity with the loose premix.

A 100% solids silicone resin, Dow Corning DC 7145, catalyzed with 3% dicumyl peroxide (Hercules Powder Company) was the basic resin of the formulation used. The blender jacket was heated to a temperature of 150°F. after the dicumyl peroxide had been dispersed in the resin. Silicone based premixes were molded by direct charging into the mold cavity. Excessive resin flow of this system prevented preforming in the wet state, while lengthy resin cure times made B-staging impracticable.

Early attempts to mold a 50% glass flake-silicone resin premix were unsuccessful. Apparently, an inhibition of curing of the silicone resins was responsible for the test molding of laminates having very poor strength. It is believed that a lag between the time of mixing the premix and the time of molding was responsible for the observed lack of proper curing. Successful molding of the silicone premixes was performed immediately after its preparation and with extreme care taken to exclude air from the mix.

#### IV.3.4.1.1.1. Compression Molding of Glass Flake Premixes for Thickness Studies

In Table 29 curing parameters are presented for each of the resin binder systems used. In most cases, manufacturers' recommended curing procedures were followed.

Previously experienced problems of incomplete cure of silicone laminates were resolved by molding premixes immediately after mixing, thereby limiting catalyst degradation by minimizing exposure of the premix to air.

TABLE 29

Molding Parameters of Various Resin Binders for Thickness Studies

	Epoxy EL-19 Series	Polyester PL-3 Series	Phenolic PHL-4 Series	Silicone SL-3 Series
Molding Temperature	300°	200°	350°	300°
Molding Pressure, psi	480	48	750	Contact
Molding Time, minutes	60	5	60	960 min.
Post Molding Cure	-	-	-	7 days @ 250°

The silicone resin systems were molded in the 7" x 7" compression mold mounted in the Watson-Stillman press. The resin binder system (Dow Corning R-7145) exhibited a tendency to stick to the chrome-plated polished mold surfaces, necessitating repeated moldings to produce acceptable laminates. The wet non-oriented loose resin glass flake mass was charged directly into the hot mold and cured using the following conditions: 450 pounds pressure (on the 4-1/4" Ram); mold temperature, 300°F.; time, 3 hours (2" or thicker cured 4 hours). Relatively low molding pressures were used because excessive drain-off of the very fluid silicone resins was encountered at higher pressures.

Laminates ranging in thickness up to 2-3/4" have been prepared. The 2-3/4" laminate is the thickest compression molded unit produced to date and weighs approximately six pounds. This is the same weight range as the 1-3/4" - 2" thick epoxy and polyester glass flake laminates, indicating that the bulk density is adversely affected by the low molding pressures.

Compression molded flat sheets utilizing Resinox RI 4009 (Monsanto Chemical Company) pulverized phenolic resin were fabricated in thicknesses ranging up to 1-1/16" for the 50/50 systems and 3/4" for the 70/30 glass flake to resin blend. The laminates were produced by layering multiple thin (1/8") oriented preformed wafers. The preformed wafer stacks were dielectrically heated until the resin was flexible, charged into the mold, and compression molded in the 9" x 9" box mold.

The height of the stack of 18 preformed wafers required to produce the 1-1/6" laminate was 6-7 inches high. The stack would not fit into the dielectric heater or the square open mold. Therefore, the stack was split into equal parts. The first part was dielectrically heated, charged into the mold and compression molded at less than 100 psi. The second stack was placed into the dielectric heater immediately upon removal of the first stack. The compression mold was opened and the second stack added to the open mold cavity. Molding pressure was then applied. Time lapse between charging the first and second lot of wafers was less than 3 minutes.

The compression molding parameters used to prepare the phenolic laminates were: dielectric heating time, maximum, 90 seconds for the thicker preformed stacks, 45-60 seconds for thinner stacks; the molding was preformed in a 9" x 9" cavity mold mounted in the Elmes press, 37 tons pressure (800 psi) on the 4" ram was used. Temperature-time cycles were 1 hour at 250°F., 1 hour at 300°F., and 1 hour at 400°F. The mold was cooled to below 150°F. before opening for part removal.

Because of equipment limitations, thicker laminates (1.5" and 2.0") could be molded in the 50% or 70% glass flake phenolic blend systems. The 9" x 9" compression mold cavity is 1.5" deep, the daylight is 5-13/16" and the compression ram plug is 1-5/8" in length. To produce a 2" laminate in the 50/50 glass flake phenolic system would have required a stack of wafers approximately 11" high (before compression).

Additional flat laminates were prepared using the preformed dry blend phenolic glass resin system. These flat laminates were molded in the 7" x 7" chrome-plated mold and were used to determine the shrinkage of the system. Phenolic laminates which were made in the 9" x 9" open form mold were not suitable because of mold construction for use in the shrinkage study.

#### IV.3.4.1.1.2. Preparation of Samples for Mechanical Testing

It was noted that preparation of specimens cut from thicker slabs required the shaving of the samples to a maximum 5/8" thickness. A Brown & Sharpe Universal Miller equipped with a spiral slab milling cutter was normally used to machine a layer of equal thickness from both sides of the thick slab as required by ASTM procedures.

Because of poor laminate quality the thicker laminates molded in the phenolic (dry blended) and silicone resin systems were not submitted for evaluation of physical properties. It was determined that attempts at milling these sheets to reduce the thickness to conform with test specimen size requirements result in major visible defects in the specimen. In some cases, complete destructive delamination resulted, for example, large portions of the laminate were pulled from the laminate face by the action of the cutter or deep cracks from the surface into the laminate were formed.

The phenolic laminates exhibited a tendency to delaminate in layers; each layer interface corresponding to the preformed wafer surfaces. The silicone laminates exhibited a tendency to delaminate in small sections of varied thickness leaving large craters in the laminate surface. The delamination apparently occurs in areas of disorientation and is the result of resin failure.

Sample thickness reduction of thick molded parts using a milling cutter produced micro chips and cracks in the laminates causing deterioration of strength properties.

Reviewing data in Table 30 pertaining to the EL-19 series, laminates 11 through 15, there is evidence of a correlation of sample thickness (increases from .250 to 2.125) and tensile strength (decreases from 9,340 psi to 5,200). This apparent relationship may in fact be due to tiny cracks developed in the test specimen during preparation, since there is no other correlation of strengths to thicknesses apparent for either resin binder system.

#### IV.3.4.1.1.3. Physical Properties vs. Laminate Thickness

In Table 30 the effect of molded thickness on physical properties is summarized for the epoxy based system at 50% and 70% glass content and the polyester resin based laminates at the 50% glass content. During preparation of the 70% glass laminate samples for physical testing, all but the 1/4 inch thickness moldings cracked or delaminated. We were unable to obtain data on any of these samples.

In general, all mechanical properties of laminates presented in Table 31 are lower than those previously obtained for thin sheets (0.060-0.150 in thickness). The low strength values obtained are

TABLE 30

Summary of Physical Properties as a Function of Compression Molded Thickness  
of Glass Flake Laminates - Epoxy & Polyester Binders

Laminate Identification	Molded Thickness, Inch	Glass Flake Content %	Average Tensile		Average Flexural		Average Compressive		Izod Impact ft-lbs/inch notch	Resin Binder
			Strength psi	Modulus psi	Strength psi	Modulus psi	Strength psi	Modulus psi		
EL-19-11	0.250		9340	2.8x10 <sup>6</sup>	14,000	2.8x10 <sup>6</sup>	25,500	.65x10 <sup>6</sup>	.66	
EL-19-12	0.875		6810	2.0x10 <sup>6</sup>	13,400	2.7x10 <sup>6</sup>	22,500	.41x10 <sup>6</sup>	.72	
EL-19-13	1.125	50	5770	1.7x10 <sup>6</sup>	16,600	1.7x10 <sup>6</sup>	21,600	.43x10 <sup>6</sup>	.60	Epoxy
EL-19-15	2.125		5200	1.8x10 <sup>6</sup>	15,300	1.8x10 <sup>6</sup>	20,000	.49x10 <sup>6</sup>	.53	
EL-19-16	0.250		2940	2.0x10 <sup>6</sup>	12,100	1.4x10 <sup>6</sup>	13,600	.84x10 <sup>6</sup>	.93	
EL-19-17	0.500	70	3800	2.4x10 <sup>6</sup>	14,000	1.8x10 <sup>6</sup>	17,000	.83x10 <sup>6</sup>	1.0	Epoxy
EL-19-18	1.000		4840	-	13,300	4.5x10 <sup>6</sup>	24,700	.80x10 <sup>6</sup>	.88	
EL-19-19	2.000		3100	2.1x10 <sup>6</sup>	12,900	1.9x10 <sup>6</sup>	19,200	.71x10 <sup>6</sup>	.86	
PL-3-6	0.250		1450	-	3,700	-	5,500	.24x10 <sup>6</sup>	.51	
PL-3-7	0.500		649	-	943	-	6,540	.43x10 <sup>6</sup>	.30	
PL-3-8	1.000	50	800	-	2,800	-	9,070	.30x10 <sup>6</sup>	.48	Polyester
PL-3-9	2.000		520	-	810	-	5,010	.30x10 <sup>6</sup>	.31	
PL-3-10	0.250		1900							
PL-3-11	0.500	70								Polyester
PL-3-12	1.000									
PL-3-13	2.000									

Samples delaminated during  
Milling - Not Tested

TABLE 31  
Physical Properties of E-glass Laminates

Sample Identification	% Glass Flake	Glass Flake Size	Tensile Str. $\times 10^3$ psi Average	Standard Dev. $\times 10^3$	Tensile Mod. $\times 10^3$ psi Average	Standard Dev. $\times 10^3$	Flexural Str. $\times 10^3$ psi Average	Standard Dev. $\times 10^3$	Flexural Mod. $\times 10^3$ psi Average	Standard Dev. $\times 10^3$	Compressive Str. $\times 10^4$ psi Average	Standard Dev. $\times 10^3$	Compressive Mod. $\times 10^4$ psi Average	Standard Dev. $\times 10^3$	Sample Identification
PH 2-2	70	Uncl.	10.3	2.4	3.96	-	2.53	2.0	5.46	0.06	1.5	5.8	3.3	1.61	PH 2-2
PH 2-3	70	Uncl.	9.3	1.3	4.95	-	1.76	7.5	4.96	-	1.5	-	1.8	-	PH 2-3
PH 3-1	50	Uncl.	8.1	2.2	2.24	-	2.16	3.5	3.91	0.25	0.9	5.8	2.3	-	PH 3-1
SL 3-3	50	Uncl.	0.8	-	-	-	3.1	0.7	3.0	0.47	0.5	0.96	2.9	2.2	SL 3-3
PH 2-3*	70	Uncl.	7.3	.96	2.48	-	-	-	-	-	0.6	1.09	2.8	-	PH 2-3*

Molding Schedule				
Preheat	P	T <sub>1</sub> <sup>o</sup>	T <sub>2</sub> <sup>o</sup>	T <sub>3</sub> <sup>o</sup>
PH 2-2	37T	250°F	1 hr	300°F 1 hr
PH 2-3	120 sec.	37T	250°F 1 hr	300°F 1 hr
PH 3-1	90 sec.	37T	250°F 1 hr	300°F 1 hr
SL 3-3	Wet Premix	P	T <sub>1</sub> <sup>o</sup>	T <sub>2</sub> <sup>o</sup>
		0	300°F	3 hrs

\*\*PH - phenolic laminates  
SL - silicone laminates

\* Milled sample

Supplement to Table 31

95% Confidence Limits

	95% CL Tensile Str. $\times 10^3$	95% CL Flex. Str. $\times 10^4$	95% CL Flex. Mod. $\times 10^6$	95% CL Comp. Str. $\times 10^4$	95% CL Comp. Mod. $\times 10^5$
PH 2-2	13.3 $\leftrightarrow$ 7.3	2.85 $\leftrightarrow$ 2.21	5.38 $\leftrightarrow$ 5.34	2.2 $\leftrightarrow$ 0.8	5.3 $\leftrightarrow$ 1.3
PH 2-3	11.4 $\leftrightarrow$ 7.2	2.95 $\leftrightarrow$ .57	-	-	-
PH 3-1	10.8 $\leftrightarrow$ 5.4	2.59 $\leftrightarrow$ 1.73	4.22 $\leftrightarrow$ 3.60	1.6 $\leftrightarrow$ 0.2	-
SL 3-3	-	3.21 $\leftrightarrow$ 2.99	3.75 $\leftrightarrow$ 2.25	0.6 $\leftrightarrow$ 0.4	5.6 $\leftrightarrow$ 0.2
PH 2-3	8.8 $\leftrightarrow$ 5.8	-	-	0.8 $\leftrightarrow$ 0.4	-

attributable to non-uniform orientation of the glass flake in the laminate. At the 70% glass content orientation of wet mixes is not possible, whereas using dry blending techniques, flat preformed oriented sheets can be produced. We believe the flake orientation contributed to higher mechanical properties.

The physical properties of the flat sheet laminates utilizing silicone and phenolic resin binder systems are presented in Table 31 and shrinkage study data is presented in Table 32.

Initial analysis of test data indicated that the phenolic laminates PH2-2, PH2-3, and PH3-1 exhibit higher tensile strength, tensile modulus, flexural strength, and flexural modulus than laminates prepared with epoxy resins. The compressive strength of these laminates are lower than those exhibited by the epoxy resin.

The high tensile and flexural results were unexpected because the poor visual appearance and milling characteristics of the laminates do not indicate high strength properties. The surface of the phenolic laminates are good and a high gloss, smooth surface is obtained giving the impression of a resin rich layer. The center of the laminates appear to be highly oriented and fully compressed. The outer edges are of poor quality, being opaque, pearl opalescent, and sometimes resin-dry and resin-rich in spots. Examination of the edges of the laminates permits easy delineation of the individual inter-wafer boundary lines. In many cases, the edges were not fully bonded. Even in the better laminates, the presence of an apparent resin-rich layer between wafers was noticed.

The tensile strength of the laminate is not as dependent upon inter-layer bond strength as are the other physical properties evaluated. The potential flexural strength range is only indicated by the reported values. The compressive strength and shear strength of the laminates are dependent upon inter-layer physics and, therefore, are poor because of the poor inter-wafer properties exhibited by the laminates. Match metal close tolerance molds and higher laminating pressure might yield higher inter-wafer strengths.

#### IV.3.4.1.2. Dry Blended Premixes

As reported earlier, a method was developed by which glass flakes could be coated by static charge inducement with a pulverized, catalyzed, B-stage epoxy resin system. It was felt that the blending method was quite satisfactory, but that developments in molding techniques were necessary to produce flat cured sheets. It has often been observed that apparently poor visual quality coincides with poor strength properties and wide variations in strengths. Obstacles to progress in obtaining high quality sheets from dry blends were resolved.

The most important variable associated with the production of acceptable quality dry blended cured laminates was the molding pressure.



TABLE 34  
Resin-Glass Flake Shrinkage Study Data

RESIN	Glass Content	<u>Length (a) Shrinkage (b)</u>		<u>Length (a) Shrinkage (b)</u>		<u>Length (a) Shrinkage (b)</u>		<u>Length (a) Shrinkage (b)</u>	
		EPOXY		POLYESTER		SILICONE		PHENOLIC	
		50%		50%		50%		50%	
<u>Front</u>									
Sample #1		7.003	.0042	7.007	.0037	7.007	.0037	7.014	.0027
#2		7.003	.0042	7.006	.0039	7.012	.0030	7.009	.0034
#3		7.002	.0044	7.005	.0040	6.998	.0050		
<u>Rear</u>									
Sample #1		7.001	.0041	7.003	.0037	7.003	.0037	7.005	.0036
#2		7.000	.0042	7.001	.0041	7.009	.0034	7.004	.0037
#3		6.997	.0046	7.001	.0041	6.996	.0048		
<u>Glass Content</u>									
		70%		70%		70%		70%	
<u>Front</u>									
Sample #1		7.003	.0042	7.010	.0033	7.014	.0027	7.012	.0030
#2		7.006	.0038	7.009	.0034	7.014	.0027		
#3		7.004	.0041	7.007	.0037				
<u>Rear</u>									
Sample #1		7.001	.0041	7.006	.0034	7.008	.0031	7.007	.0037
#2		7.001	.0041	7.005	.0036	7.009	.0030		
#3		7.000	.0046	7.004	.0037				

7" x 7" box mold dimensions - Front Rear

(a) Inches

(b) Shrinkage Inch/Inch

7.033 7.030

Using a compression mold and high molding pressures (30 tons = 740 psi) resulted in the preparation of void-free clear laminates. Resin systems were developed which were amenable to this manufacturing process. These systems had to be pulverized easily into fine powders; free from reagglomerating into lumps during blending, have sufficiently low flow times during curing to aid in glass flake wet-out. These characteristics had to be tempered and compatible with strength and toughness criteria in the final laminate.

A study was started to determine the best set of molding conditions as evidenced by laminate quality and strength. The majority of the laminates were prepared using E-15 B-staged epoxy resin system. The solid epoxy resins were investigated in order to utilize a mechanical mixture of a pulverized resin and a pulverized hardener. One of these systems, Jones Dabney Epi Rez 522, a solid epoxy with a 65-70°C. melting point, combined with pulverized metaphenylene diamine indicated more promise toward increased tensile strength values than the E-15 resin system previously described.

In Table 33 the molding variables are summarized for the preparation of laminates EL-15-18 through EL-15-38, and EL-25-1 and EL-26-1, 2. Table 34 presents tensile strength and glass content for these same laminates. A summary of the recommended molding parameters for dry blended epoxy premixes that evolved from the study is presented in Table 35.

Test plates were apparently void-free according to their density determinations. Differences in visual textures were probably caused by misorientation of the glass. These differences appeared as slightly opaque spots, lines and swirls. Also, a few of the visual lines and spots were caused by "clumping", that is, narrow regions of resin-glass non-homogeneity (Photograph 10). Their appearance is similar to a "knit line" which is produced in injection molding by two flowing streams meeting and not fusing entirely at the contact points.

The tensile values of the test strips cut from the molded sheets were encouragingly high. The tensile strips were visually examined for flaws, especially the position of the largest flaw in the strip. In most cases, the position of the largest flaw determined the point of rupture.

One tensile piece, EL-23-4, in which the smallest number of flaws was found, had the highest tensile value obtained to date (22,900 lbs. per sq. inch). The average tensile strength values of the test strips from EL-23-4 and 6 sheets were 19,100 and 16,000 lbs. per sq. inch, respectively. The average flexural strength values of 23,800 and 28,400 lbs. per sq. inch were low for corresponding tensile strength values. (Flexural strength values are expected to be twice the tensile strength values.) The standard deviations of the tensile strength values varied from 1,200 to 2,700 lbs. per sq. inch. No standard deviations were calculated for the flexural strength values as less than five samples were used for testing. The tensile moduli, or moduli of elasticity values in tension, varied from 5.3 to  $7.1 \times 10^6$  lbs. per sq. inch. The flexural strength moduli values were between 2.9 and  $4.0 \times 10^6$  lbs. per sq. inch.

TABLE 12  
SUMMARY OF PREFORMING AND MOLDING PARAMETERS FOR  
DRY SHEETS OF GLASS-FIBER AND EPOXY RESIN SYSTEM

Laminate Identifi.	Preforming Parameters				Molding Parameters				Comments	% Glass	Sheet Appear- ance	Resin Type	Resin Formulation Typical Wt.	Resin Repair & Mixing Size
	$P_T$	$P_D$	$P_F$	Mo. of Preforms	$C_T$	$C_D$	$M_T$	$M_D$						
EL-15-18	220	90	C	2	220	1.5	220-370	45	30	Stratified edges	70	C	JDS10 MFD	100 14
-19	170	15	250	2	220	1.5	220-370	45	30	Backed mold plate - not tested - warped sheet	50	B	Epoxy Aniline Cured	1
-20	170	15	250	2	220	1.5	220-370	45	20	Slightly cloudy	50	B		
-21	170	30	250	1	220	1.5	220-370	45	15	Clear sheet	50	B-A		
-22	170	30	250	2	220	1.5	220-370	45	30	Good	60	A		
-23	170	30	250	1	220	1.5	220-370	45	30	Good	60	A		
-24	160	15	200	1	170	0	170	45	30	Clear; corner-dry edges Not tested	80	D	JDS10 MFD	100 14
-25	160	30	200	1	220	0	220	45	30	Poor handle flow-not tested	80	C	Epoxy Aniline Cured	1
-26	170	-	200	1	350	0	350	10	30	Exteriorly welded - not tested	80	C		
-27	160	20	200	0	-	0	370	45	30		70	B-C	JDS10 MFD	100 14
-28	160	20	200	0	-	0	320	45	30	Clear; some scorching spots	70	B	Epoxy Aniline Cured	1
-29	160	20	200	0	-	0	270	45	30	Good sheet	70	A		
-30	160	20	200	1	240	0	240	45	30		70	B	JDS10 MFD	100 14
-31	160	20	200	1	270	1.5	270	35	30	Dry corners	70	B	Epoxy Aniline Cured	1
-32A	160	20	200	3	270	2	270	35	30	Good; p. wrinkles in corners; 22A post-cured 2 hrs. at 350°F	70	A		
-32B	160	20	200											
-33	160	30	200	1	270	0	270	35	30	Poor edges. Not tested	80	C	JDS10 MFD	100 14
-34	160	30	200	2	270	1.5	270	35	30	Fair appearance	80	B	Epoxy Aniline Cured	1
-35	160	30	200	2	270	2.5	270	35	30	Poor - not tested	80	C-D		
-36	160	30	200	2	270	2.5	270	35	30	Poor - not tested	80	C-D		
-37	160	30	200	2	240	0	240	2 hr	30	Excellent sheet	70	A	JDS10 MFD	100 14
-38	160	30	200	2	370	0	370	2 hr	30	Excellent sheet	70	A		
EL-25-1	-	-	-	0	350	0	350	45	30	Variegated appearance	70	B-C	JDS60 JDS09 MFD	60 40 6.7
EL-26-1	170	20	200	2	100	0	300	2 hr	30	Excellent sheet	70	A	JDS22 MFD	100 1.9
EL-26-2	170	20	200	2	100	0	300	2 hr	30	Excellent sheet	70	A		

TABLE 34

GLASS CONTENT, LAMINATE THICKNESS AND TENSILE  
 PROPERTIES OF COMPRESSION MOLDED DRY BLENDS-EPOXY BINDER

	% $G_i$	% $G_f$	$T_s$	$\sigma$	$h$	$T_m$	$\delta$	Laminate Thickness Inches
EL-15-18	70	70	15.3	1.60	6	5.72	1.5	0.100
20	50	49.8	14.1	2.1	5	3.67	1.0	0.120
21	50	49.6	14.0	3.2	5	3.42	0.6	0.050
22	60	59.2	10.8	2.3	6	3.50	-	0.080
23	60	59.7	10.1	2.5	5	4.92	-	0.050
27	70	70.9	15.0	3.5	5	4.78	0.48	0.040
28	70	70	13.7	3.0	6	5.54	1.9	0.040
29	70	70	12.9	3.8	6	5.20	-	0.040
30	70	70.3	12.9	3.0	6	3.50	0.57	0.050
31	70	70.5	14.1	1.5	6	4.90	0.51	0.040
32A	70	70.4	12.0	-	3	4.52	-	0.140
32B	70	70.6	10.5	-	3	6.62	-	0.140
34	80	80.4	13.2	-	3	9.63	-	0.090
37	70	69.8	16.2	3.9	7	5.48	0.49	
38	70	70.1	15.0	1.9	7	5.52	0.77	
EL-25-1	70	-	12.4	-	4	6.39	-	
EL-26-1	70	-	17.0	2.2	11	-	-	

Supplement to Table 3495% Confidence Limits

	<u>95% CL Tensile Str. <math>\times 10^3</math></u>	<u>95% CL Tensile Mod. <math>\times 10^6</math></u>
EL 15-18	17.0 $\leftrightarrow$ 13.6	7.34 $\leftrightarrow$ 4.10
EL 15-20	16.7 $\leftrightarrow$ 11.5	4.91 $\leftrightarrow$ 2.43
EL 15-21	18.0 $\leftrightarrow$ 10.0	4.16 $\leftrightarrow$ 2.68
EL 15-22	13.2 $\leftrightarrow$ 8.4	-
EL 15-23	13.2 $\leftrightarrow$ 7.0	-
EL 15-27	19.3 $\leftrightarrow$ 10.7	5.38 $\leftrightarrow$ 4.18
EL 15-28	16.9 $\leftrightarrow$ 10.5	7.54 $\leftrightarrow$ 3.54
EL 15-29	16.9 $\leftrightarrow$ 8.9	-
EL 15-30	16.0 $\leftrightarrow$ 9.8	4.10 $\leftrightarrow$ 2.90
EL 15-31	15.7 $\leftrightarrow$ 12.5	5.44 $\leftrightarrow$ 4.36
EL 15-37	19.8 $\leftrightarrow$ 12.6	5.93 $\leftrightarrow$ 5.03
EL 15-38	16.7 $\leftrightarrow$ 13.3	6.23 $\leftrightarrow$ 4.81
EL 26-1	18.5 $\leftrightarrow$ 15.5	-

## Key to Table 34

1.  $\% G_1$   
Weight per cent of glass flake formulated in dry blend.
2.  $\% G_f$   
Weight percentage of glass flake in final laminate -  
determined by analysis.
3.  $T_s$   
Average tensile strength, thousand psi.
4.  $\sigma$  = Standard deviation of tensile strength values, thousand psi.
5.  $n$  = no. of tensile samples used in calculation of  
standard deviation.
6.  $T_m$  = Average tensile modulus, million psi.
7.  $\sigma$  = Standard deviation of tensile modulus, million psi.

Table 35

SUMMARY OF RECOMMENDED MOLDING PARAMETERS FOR EL-15 SERIES

<u>Preforming</u>			<u>Molding Cycle</u>				
P <sub>T</sub>	P <sub>θ</sub>	P <sub>p</sub>	C <sub>T</sub>	C <sub>θ</sub>	M <sub>T</sub>	M <sub>θ</sub>	M <sub>p</sub>
160-170	15-30	200-250	240-370	0-2	240-370	2	30

Key:P<sub>T</sub> = Preforming temperature, °F.P<sub>θ</sub> = Preforming time, secondsP<sub>p</sub> = Preforming pressure, psiC<sub>θ</sub> = Time in which preformed dry blend is allowed to come to molding temperature at contact pressure, subsequently referred to as contact time, minutes.C<sub>T</sub> = Contact temperatureM<sub>T</sub> = Molding temperature, °F.M<sub>θ</sub> = Molding time, hrs.M<sub>p</sub> = Molding pressure on 4 1/2 inch ram, tons

## Key to Tables 35 and 36

## 1. Preforming Parameters

$P_T$  = temperature used for preforming in 9 x 9 compression mold, °F.

$P_\theta$  = time that dry blend is formed to reduce its bulk, seconds.

$P_p$  = preform pressure, psi  
(pressure on 4" ram)

$c$  = contact pressure

## 2. No. of Preforms

Refers to the number of preforms which were stacked together in the mold before molding.

## 3. Molding Parameters

$C_i$  = contact time, minutes, °F. (temperature of mold when preform is inserted)

$C_\theta$  = contact time, minutes  
(time in which the preform is allowed to come to the molding temperature under contact pressure)

$M_T$  = molding temperature, °F.

$M_\theta$  = molding time, minutes

$M_p$  = molding pressure, tons on 4 inch ram

## Additional:

All preforms were 9 x 9 inches.

All compression molded sheets were 9 x 9 inches.

## 4. % Glass

Refers to the weight percentage of glass flake formulated in the dry blend.

## 5. Sheet Appearance

A. Excellent sheet quality, translucent, no voids, no dry spots, minimum flow patterns at edges of sheet.

B. Good sheet quality, translucent, no voids, no dry spots, some flow patterns at edges of sheets, some color variation throughout sheet



- C. Fair sheet quality - translucent - cloudy in center, opaque and dry spots at edges, incomplete resin flow.
- D. Poor sheet quality - cloudy areas, dry spotting, poor resin flow, blister formation.
- E. Extreme blistering, delamination, no resin flow or translucent areas.

#### 6. Resin Formulation

a. Resins	Wt/Epoxide
JD 510 - Jones Dabney Epi-Res 510	185-200
JD 509 - Jones Dabney Epi-Res 509	185-200
JD 560 - Jones Dabney Epi-Res 560	3,500-5,500
Mixture 60% 560 40% 510	448
JD 522 - Jones Dabney	550-650
R5655 - Reichold Chemical Co. Plyophen Pulverized Phenolic Resin Contains Own catalyst	
ERRB 0100 - Union Carbide Plastic Epoxidized Novolak	
L-4180 - American Cyanamid Alkyd Resin Laminac 4180 self catalyzing	
CY405 - American Cyanamid Melamine Resin Cymel 405 self catalyzing	

#### b. Hardeners

MPD - metaphenylene diamine  
DADS - diamino diphenyl sulfone

#### 7. Resin Preparation and Mixing

1. Resin blended with catalyst allowed to "B stage" at room temperature for 24 hours, micropulverized and classified into -100 mesh fraction.
2. Resins heated and blended, allowed to solidify at room temperature, resin then pulverized into -100 mesh fraction and mechanically mixed with pulverized catalyst.

3. Solid resin pulverized to -100 mesh then blended with pulverized catalyst.
4. Resin is purchased pulverized and catalyzed. One package powder added to glass flake.

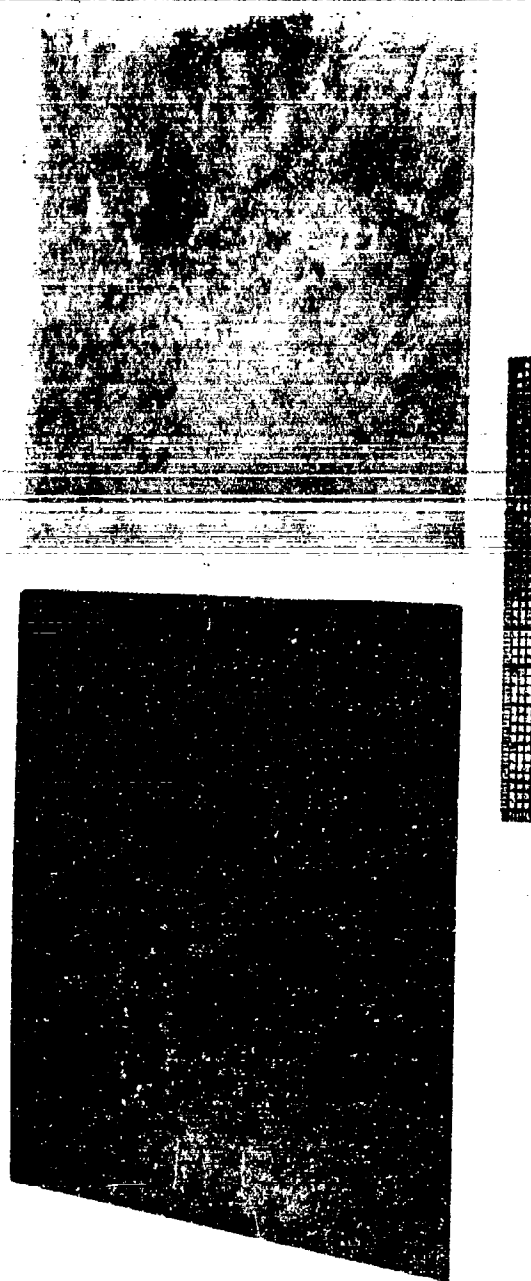
**Dry Blending Procedure:**

Glass flake is charged into Patterson-Kelly blender and rotated for 1/2 hour.

Resin system is then added and tumbled for 2 hours.

**Glass Size:**

U - Unclassified



Photograph 10

Molded Appearance Comparison of an Epoxy-Glass Flake Sheet Oriented and Degassed (left) and an Unoriented Sheet (right) that has not been Degassed.

#### IV.3.4.1.3. Other Resin Systems

The encouraging results obtained with the compression molding of epoxy systems led us to a preliminary screening of phenolic, Novalak-epoxy, alkyd and melamine resin systems. Data obtained in this study are presented in Tables 36 and 37.

A Reichold Chemical Company catalyzed phenolic-aldehyde resin, Plyophen 5655, was dry blended with 16 to 50 mesh to yield a mixture containing 50% glass flake. The mixture was pressed in a 9" x 9" sheet mold at 160°F. for 10 minutes at about 200 lbs. per sq. inch. No flow or fusion occurred. Then it was pressed at about 300 lbs. per sq. inch for 3 minutes at a platen temperature of 370°F. The mold was opened to release the gas and steam. Then the curing was completed at about 700 lbs. per sq. inch pressure for 10 minutes at 370°F. The sheet upon removal from the hot mold raised blisters. There were many voids in the center. The sheet was too poor to test. (Pressures of 2,000 psi are usually used in molding of phenolics.) Two other compression moldings made with preformed material showed no promise and were not tested.

A Novalak-epoxy resin, Union Carbide's ERRB 0100, catalyzed with diamine diphenyl sulfone appears unsuitable for use. Compression molding of a 70% glass content gave rise to blistering from volatile release during curing.

A catalyzed alkyd resin laminate, Laminac 4180, was ground to pass through a 100 mesh screen. Even though the resin had a sharp melting point of 195°F., it did not flow profusely in the mold over a range of curing temperatures. The sheet did not cure evenly and some sections were tacky at room temperature. There were many voids. The sheet was too poor to test.

A catalyzed melamine resin, American Cyanamid's Cymel 405, was dry blended with unclassified glass flake. The 70% glass flake mixture was compression molded at 350°F. for 10 minutes at a pressure of 700 lbs. per sq. inch. Very poor bonding of the glass flake occurred and the sheet had many voids and gas blisters. The sheet was not tested.

#### IV.3.4.1.4. Conclusions

During the mixing and processing method studies, epoxy resins were chosen for binders predominantly. It was known that the use of epoxy resins had resulted in best strength properties of glass flake laminates. It was deemed expedient to concentrate on the epoxy systems in order to realize the best mixing method for development of high strength laminates and to provide a basis for measurement of potential process improvement. Since handling properties of the polyester, silicone and phenolic resin/glass materials are similar, it was planned to develop all handling and molding techniques using epoxy resin binders and then use these same techniques for the other resin systems.

TABLE 36

## SUMMARY OF PREFORMING AND MOLDING PARAMETERS FOR

DRY BLENDS OF GLASS-FLAKE AND PHENOLIC, EPOXY NOVALAK, ALKYD and MELAMINE RESIN SYSTEMS

Laminate Identification	P <sub>I</sub>	P <sub>0</sub>	P	No. of Pre-Forms	C <sub>I</sub>	C <sub>0</sub>	M <sub>I</sub>	M <sub>0</sub>	M <sub>P</sub>	Comments	% Glass	Sheet Appearance	Resin Type	Resin Formulation Typical Wt.	Resin Preparation and Mixing	Glass Size
PH-1-1	0	0	0	0	350	0	350	10	30	Blisters formed. Some clear sections	50	D		R 5655-100	4	
PH-1-2	270	5	200	2	380	1.5	380	10	30	Blisters, Delamination, very porous	50	F	Phenolic			
PH-1-3	270	5	200	2	380	0.5	380	10	30	Blisters, Delamination, Very porous	50	F				
ENL-24-1	0	0	0	0	350	0	350	60	30	Dry Spots, Blisters. Some clear spots	70	D	Novolak-Epoxy	ERRB-0100 DADS	3	U
AL-1-1	0	0	0	0	190	30	190	10	30	No clarity, porous Blisters formed	50	D-F		L4180-100	4	U
-2					190	30	190	10	30		60	D	Alkyd			
-3					370	30	370	10	30		60	D				
-4					270	30	270	10	30		60	D				
ML-1-1	0	0	0	0	350	0	350	10	30	Blisters formed	70	D-F	Melamine	CY 405-100	4	U

Table 37

## SUMMARY OF NON-EPOXY RESIN BINDER LAMINATES

Laminate Identification	Formulation	Glass Size	Tensile Strength psi x 10 <sup>-3</sup>		Laminate Density Gr/cc	Glass Content
			Average	Range		
SL-2-1	DC 7146 DiCup R 1%	U	2.95	2.42-3.44	----	----
PL-3-1	L 4128 Benz. P 1%	U	2.19	1.16-3.70	1.77	67.2
PL-3-2	L 4128 Benz. P. 1%	U	2.60	2.2-3.90	1.43	58.9

Key:

DC 7146 - Dow Corning 7146 Silicone Resin

L 4128 - Laminac 4128 - Polyester Resin - American Cyanamid Co.

Benz. P. - Benzoyl Peroxide - Cadet Chemical Co.

DiCup R - Recrystallized Dicumyl Peroxide - Hercules Powder Co.

U - Unclassified Glass Flake

Laminate formulation using phenolic resin binders have been hindered because of apparent high exothermic curing and volatile formation during curing as a result of methylation.

The silicone and polyester laminates prepared were of poor quality and had low strength properties, in part the result of difficult curing technique, and in part by inability to utilize preforming and flake orientation premold processing. Milling of laminates to prepare physical test specimens is highly detrimental to the test specimen.

#### IV.3.4.1.5. Experimental Molding of Complex Shapes

A variety of complex shapes were compression molded experimentally using epoxy resin binders. A description of the shapes, cycles and compositions used are given in Table 38. The molded shapes are shown in Photographs 11, 12, 13 and 14.

In the compression molding of most of the complex shapes, the orientation of the glass flake is not readily precontrolled since there is usually turbulent flow of material within the mold cavity. As a result, for all shapes fabricated in this section, no effort was made to preorient the premix.

Premixes containing 50% and 60% glass fabricated at the free floating ram pressure were molded into shapes having complex curves. The cavity fill was excellent, but there were some void spots, probably due to trapped gas. The piece molded with 70% glass flake was rather porous and did not have the translucency that the 50% and 60% pieces had. This would indicate that a higher molding pressure is required to produce visual appearance equal to the 50% and 60% glass laminates.

Complex shaped circular disks (Photograph 11) were produced using B-staged calendered sheets. The molding was accomplished with no difficulty and the flake orientation was not disturbed during the process. Highly transparent quality items were produced.

A planar step piece with sharp edges at various thicknesses and parallel edges was molded from a 50% glass flake. Several pieces that were molded were mutilated in removing from the mold. The edges seemed well formed, but no conclusions could be drawn as the molding surface had not been prepared to provide release of the part without damage.

A small bevel gear was molded from a 50% glass flake mixture using a prototype epoxy mold as shown in Photograph 13. The molding pressure was limited at 200 psi. Above 200 psi, the premix would have been extruded from the top and bottom of the mold cavity. The fill-in of the glass premix at the teeth was good. The orientation of the glass flake was random as expected.

Table 38

## Molding Cycles for Complex Shapes

Mold	Starting Glass Content	Glass Size	C U R E C Y C L E S			Comments
			Time Hrs.	Temp. ° F.	Hydraulic System Press. psi	
Ash Tray	50	1	2	200	0	Excellent cavity fill Some air bubbles
			+ 6	220	0	
Ash Tray	60	1	2	200	0	Excellent cavity fill Some air bubbles
			+ 6	220	0	
Ash Tray	70	1	2	200	1500	Very porous piece produced
			+ 6	220	0	
Gear	50	2	2	200	200	Excellent replication of mold surface Some air bubbles
			2	350	0	
Step Mold	50	2	2	200	250	Dry Edges Good fill of cavity Some interior delamination
			2	350	0	
Plug	70	2	30 mins.	340	100 tons	Good cavity fill some dry and void spots



SUPPLEMENT TO TABLE 38  
PROCEDURE FOR COMPLEX SHAPES

Premix:

Composition of Resin Binder:

Jones Dabney 509 (Epoxy)	100 parts
Methyl Nadic Anhydride	95 parts
DMP-10	2 parts

Abbe Mixer Used

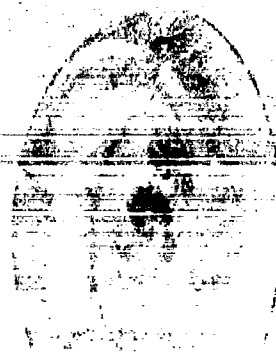
5 min. mix time  
Room temperature mix.

Material Stacked in Mold

No degassing  
No orientation

Glass Size:

1. +8 mesh	2 micron glass flake
2. Unclassified	2 micron glass flake



Photograph 11

Curved Pieces

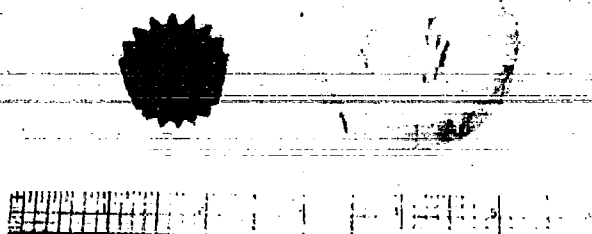
Left to Right: 70, 60, 50 Per Cent Glass

Photograph 12



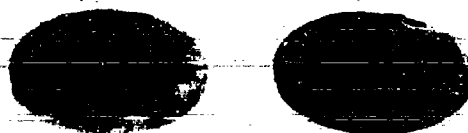
Compression Molded Planar Step Piece

## Photograph 13



Compression Molded Bevel Gear and  
Epoxy Mold

## Photograph 14



Epoxy-Glass Flake (left)  
and  
Phenol G.P. (right)  
Compression Molded Plug

One of the objectives of the compression molding study has been to evaluate the use of molds designed for plastics of the filled phenolic, urea or melamine type. A 100 ton production press equipped with a multicavity die for molding preformed general purpose phenolic molding powders, located at Futuramic Molded Products, Hartford, Connecticut, has been used in this study. Molding pressures of 100 tons are not uncommon for molding of phenolic and melamine compounds but pressures of this order had not been tried with glass flake premixes. Seventy per cent glass premix was chosen, since that glass content appeared to be difficult to mold into shapes having complex contours in attempts at lower pressures.

A 25% excess of premix was stacked into the mold cavity which had been coated with a fluorocarbon mold release compound. When molding pressure was applied, some of the excess glass-resin mixture was squeezed out. In about 30 seconds, free resin oozed out of the flash clearance section between the top and bottom cavity sections. After curing for 30 minutes, the piece was ejected with difficulty caused by liquid resin seeping down the retracting and ejecting pins which had cured and "froze" the pins. It took several retraction and ejection cycles to loosen the pins enough to eject the piece. Since this was a press currently used for production, no further molding tests were requested.

The molded piece was dense and conformed to the shape of the cavity. There was no visible orientation of the glass flake. There were some apparent dry spots as a result of resin squeeze-out. From this test, it appears possible to mold pieces with a high glass content.

Photograph 14 shows the molded glastic plug and a plug molded from a filled phenolic.

#### IV.3.4.1.5.1. Conclusions

General conclusions were derived from the experimental compression molding of glass flake (Abbe mix) premixes. Orientation of glass flakes within compression molded laminates is difficult to control to assure orientation which follows the molding contours. The orientation is more controllable when B-staged preforms are used. A polished surface is required for proper release of the molded part from the mold. Glass contents of 70% and above can be compression molded at high molding pressures. Molds used for production of other plastics, especially reinforced plastics, may be used to mold glass flake composites. Compression molded items can be prepared in an unlimited number and variety of shapes and forms. The flow properties of glass flakes are amenable to compression molding. The premix flows readily and fills all parts of the mold.

#### IV.3.4.2. Transfer Molding

Transfer molding is a variation of compression molding. The major difference being that the premix is not placed directly into the mold cavity but into a separate pot (which can be heated) outside the mold. The premix is then forced by a ram or plunger through channels from the external chamber to the closed mold cavity. The premix is cured in the closed mold cavity.

The success encountered with pilot plant compression molding of complex shapes caused us to omit attempts to develop transfer molding technique at the laboratory level. Arrangements were made to utilize production equipment to attempt to reduce this technique to practice without the intermediate expenditure. Two complex shapes were fabricated very successfully in Phase III of this contract, and are described later in this report.

#### IV.3.4.3. Extrusion

Attempts to develop an extrusion process for glass flake are covered in Phase II, Section 3 of this report.

In summary, it was determined that extrusion processing was not suitable for glass flake premixes, using the commercial resin systems being evaluated under this contract. Complete redesign of an extruder would be required, together with the development of a specialized resin system, before additional efforts could be made.

#### IV.3.4.4. Calendering

Calendering was developed into a valuable processing technique and is fully explained in Phase II, Section 3 of this report. The continuous molding of laminates using a calendering-conveyor system would be limited only by process time considerations. The cure times required before gelations and the complete cure of a reinforced plastic binder system would necessitate use of ovens, multiple heat rolls and dielectric heaters. Recognizing this factor to be the only limitation in expanding the calender process we developed to an ultimate end item capability, it was deemed unnecessary to expend the financial and manpower effort on this contract to prove our contention.

#### IV.3.4.5. Centrifugal Casting

Three variations of a centrifugal casting process were investigated under this contract. Shapes were fabricated by rotational molding, horizontal and vertical cylinder casting.

All three methods rely on centrifugal force, generated by the rotational motion of a mold to orient flake, and compress the bulk to fill all cavities with resin premix. In using these processes particular attention must be given to the quantity and viscosity of the resin systems selected. In premixes having low resin viscosities, or small quantities of glass flakes, there is a tendency for the reinforcing material, which has a higher density, to be cast to the outside surface of the molded item. Thus, in these processes, resin-rich areas appear on inside surfaces, resin starved areas on outer surfaces.

##### IV.3.4.5.1. Rotational Molding

Limited studies of rotational molding of glass flake resin blends were made utilizing a laboratory "Roto-Molder" produced by the Mercury Molding Company, Yonkers, New York.

Rotational molding units are used industrially for the molding of hollow items as dolls, balls and other novelties using vinyl plastisol compounds. A unit consists of a platform which rotates simultaneously in two directions and is enclosed in a gas-fired oven and fuse the molding compound while the mold(s) is rotating. In each plane of rotation, the molds rotate in a regular and circular direction. A batch process is used wherein the mold or molds used are filled outside of the heated rotational chamber, placed within the chamber and rotated until the plastisol is fused. Low speeds are used in these machines to provide an evenly distributed film of plastisol.

A test run was performed using a hand-kneaded premix of an epoxy resin and glass flake. After observation that the maximum rotational speed of the unit was only 16 rpm, a 10% glass, 90% resin premix was prepared in order to obtain some resin-glass flow. A 100 gram mixture was charged into a 3" diameter sphere mold and rotated for one hour at 350°F. (16 rpm about the one axis, 4 rpm about the other axis). After this one hour cycle, the ball mold was removed from the oven, opened and inspected. It was obvious from the variation in wall thickness of the sphere that very limited resin-glass flow had taken place even with the very low glass content premix. Wall thickness within the sphere varied from 0.005 to 0.250 inch.

Rotational molding machines as built do not appear suitable for the casting of flake glass pipe. Extensive redesign to achieve the required higher rotational speed would be necessary to cast high glass content material, changing the use for which the machine was designed. Rather, it has been apparent that the design and fabrication of a centrifugal casting unit imparting high rotational speeds to cast cylindrical shapes would be required.

#### IV.3.4.5.2. Vertical Centrifugal Castings

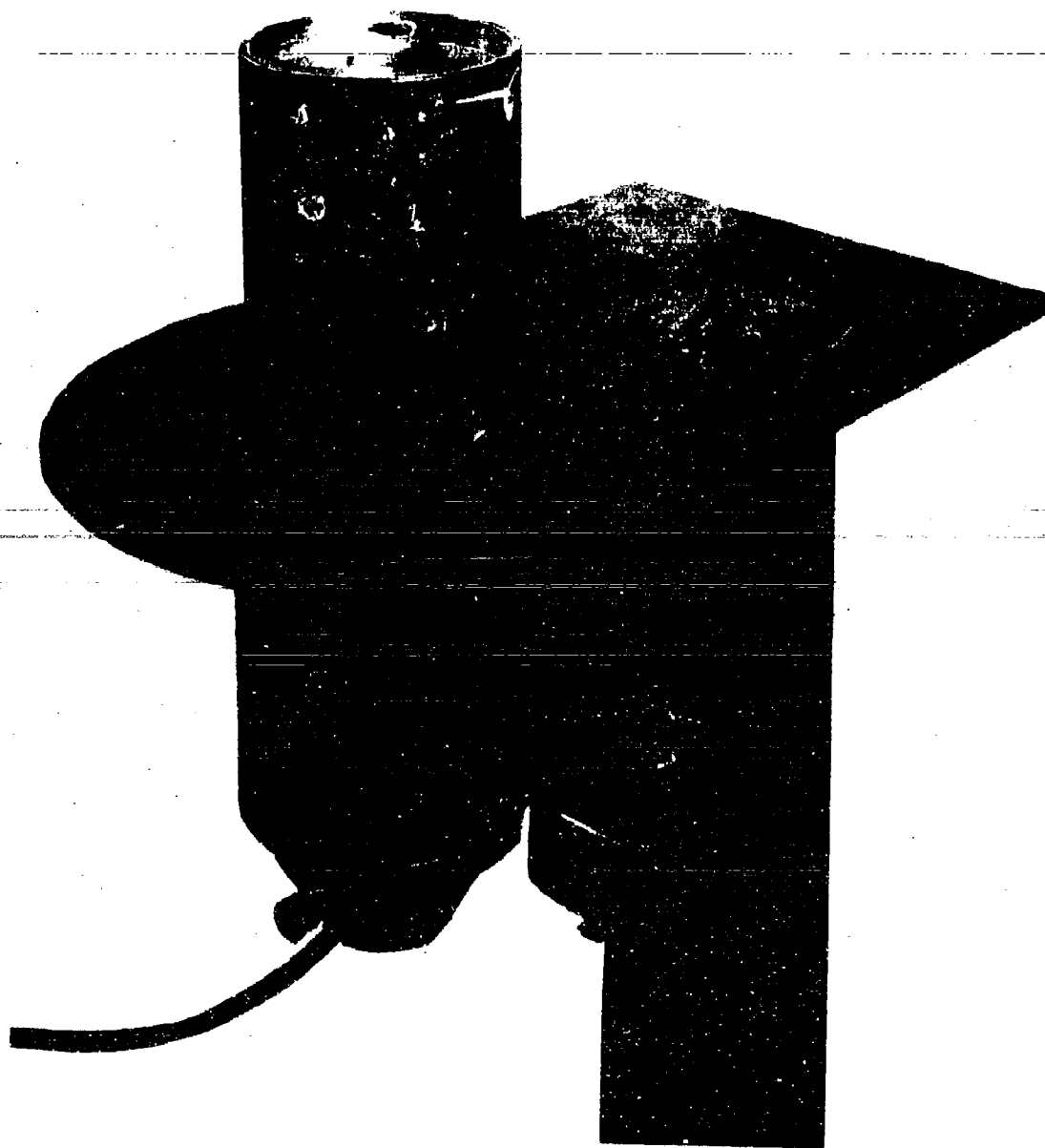
Using premixes prepared in the Abbe mixer several centrifugally cast cylindrical sections were produced. The vertical centrifuge is a 6" diameter, 11" deep unit with a 2-speed motor (Photograph 15). Cylinders were always prepared at the 4800 rpm higher speed to exert maximum G force on the flakes.

The first of two experiments utilized a premix consisting of 50% glass classified into the -8+16 mesh fraction and 50% Laminac polyester 4128 catalyzed with 1% benzoyl peroxide and 2% Laminac promoter 400 (room temperature cure system). The premix was deposited into the rotating bowl and then cast for a period of one hour until the resin had cured.

The unit exhibited drain-out from the inside diameter to the outside diameter of the cylinder. Additionally, resin had flowed entirely away from the premix and up the wall of the centrifuge. The cylinder cast with the 60% glass content premix exhibited segregation to the outside diameter of the cylinder wall due to centrifugal action upon the resin. No resin flow away from the premix up the centrifuge wall was observed at this glass content.



Photograph 15



Centrifugal Casting Unit  
(six inch diameter bowl)

Both cylinders were cast vertically and, therefore, as a result, had thicker wall sections at the bottom than at the top of the cylinder. Inside diameters were very irregular as the centrifugal force was not sufficient enough to distribute the premix evenly. Randomness of orientation of glass flake and void entrapment was very common as a cross section of the pipe revealed. The cylinder cast with 60% glass is depicted in Photograph 16. The large crack shown in the wall developed when the cylinder was released from the centrifuge.

Since no heat source could be used to provide uniform curing temperatures within the centrifuge chamber, a room temperature curing epoxy resin was used for casting flake glass cylinders. The resin system used consisted of 100 parts Jones Dabney Epi-Rez 509 or 510 and 12 parts triethylene tetramine.

One cylinder, appearing in Photograph 17 was cast with 50% glass premix. The premix was deposited in the bowl of the rotating centrifuge where it redistributed itself upon the rotating wall. An expandable mandrel was used to compress the walls further and to produce a uniform thickness wall.

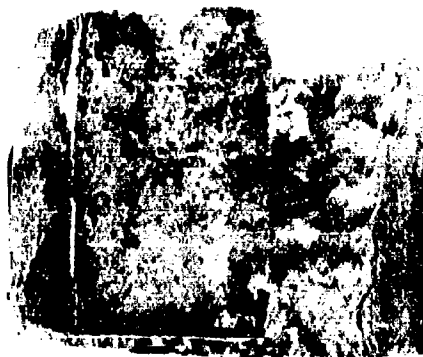
During the casting operation, resin segregation to the outside diameter of the cylinder was noted. After one hour at room temperature the cylinder was released from the centrifuge. (To aid in the release of this cylinder and succeeding ones, a destructible semi-rigid polyurethane foam approximately 3/4" thick was placed in the centrifugal bowl. After the curing and casting time, this liner was destroyed and the cylinder removed.) There is obvious random orientation of the glass flake as evidenced by the "marbled" appearance of the cylinder. The appearance and strength of this cylinder is apparently much improved over the polyester glass flake cylinders.

As a means of casting a cylinder that contained oriented glass flake, a pre-oriented sheet of 50% glass was prepared and wound into the centrifuge. This first attempt was unsuccessful due to the poor self-cohesion of the premixes and in attempting to wind the pre-oriented sheet into the centrifuge, the glass resin mix crumbled.

To eliminate the problem of sheet destruction, a preoriented sheet was prepared and chilled with dry ice. In this manner, the viscosity of the resin binder system was reduced to the point where it could be self-supporting. This cold sheet was then wound into the centrifuge, and cast for a period of one hour. During the winding of the preoriented sheet within the centrifuge, some fracturing of the sheet was noticed. As a result, the finished cylinder had some discontinuity lines running parallel to the axis of the pipe where the sheet had separated. These lines are visible in Photograph 18. Photograph 19 depicts both the oriented cylinder and the cylinder with concentric flake orientation. Table 39 presents a summary of casting data for the two cylinders.

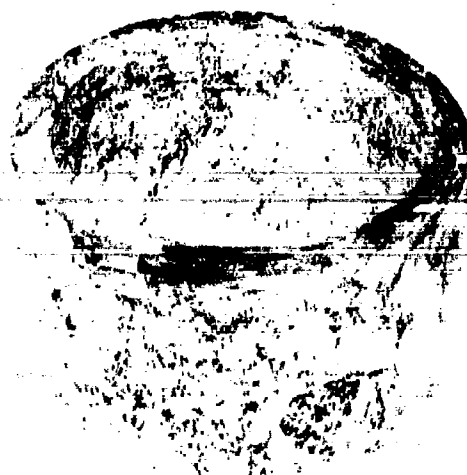
It should be noted that while the oriented cylinder was cast without the use of an expandable mandrel, the resultant wall thickness of the cylinder was not tapered as was the previous experience without the mandrel.

Photograph 16



Centrifugally Cast Polyester  
Glass Flake 6" Diameter Cylinder

Photograph 17



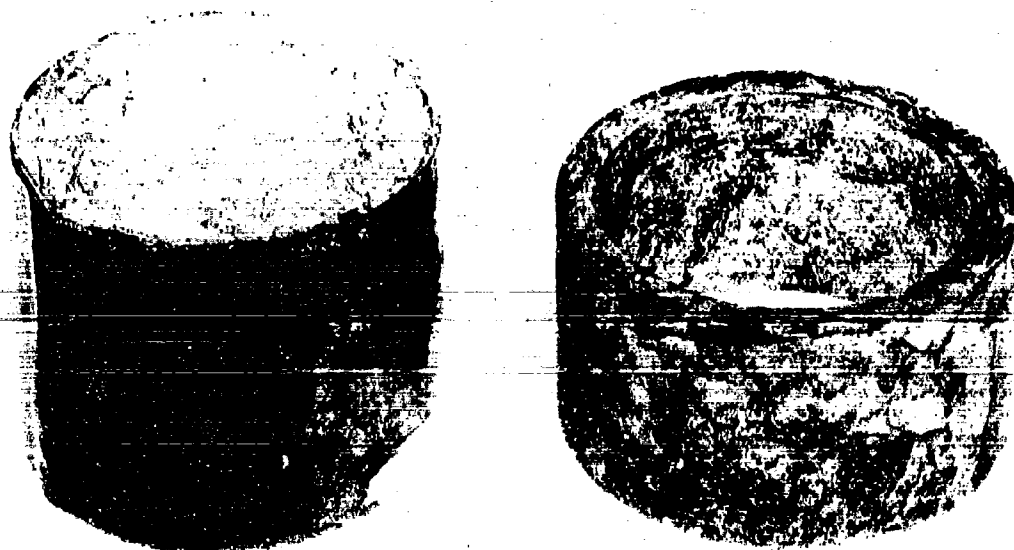
Centrifugally Cast Glass  
Clink Epoxy Cylinder

Photograph 18



Centrifugally Cast Preoriented  
Glass Flake Cylinder

Photograph 19



Random and Preoriented  
Glass Flake Cylinder

**T A B L E 39**  
**CENTRIFUGAL CASTING OF EPOXY GLASS FLAKE CYLINDERS**

Identification	Glass Orientation	CASTING VARIABLES			Composition
		r.p.m.	Time	Other	
EL 21 CP	Random	1725	1 Hr.	Expandable Mandrel	50 per cent Glass 50 per cent Resin
EL 22 CP	Preoriented	1725	1 Hr.	--	

#### IV.3.4.5.3. Conclusion

The process of centrifugal casting of pipes showed promise. The epoxy cylinders prepared from epoxy resin premixes had superior physical appearance than the polyester cylinders. The use of higher rotational speeds and higher G forces was believed to be an aid in orientation of the glass flakes in the finished cylinder. These parameters were investigated further using a horizontal centrifuge.

#### IV.3.4.6. Horizontal Casting

Trial runs were made with the horizontal centrifugal casting machine utilizing a hydraulic ram feeder to extrude and orient a ribbon of glass flake premix into the rotating casting chamber. The trial runs demonstrated the need for a mechanical leveling device (mandrel) to assure uniform inside diameter of cast cylinders. The maximum speed of the unit (4000 rpm) does not eliminate this defect. The problem was observed previously with the low speed vertical centrifuge used earlier in the program. Continued efforts to produce centrifugal cast cylinders were made using simple mandrels to overcome the non-uniformity of inside diameters, inserts to produce changes in inside and outside diameter and a slotted feed inner chamber to control feed into the centrifuge chamber.

The wet premixes were generally charged into the centrifuge. An attempt was made to uniformly deposit a 1.5-2 inch layer on the walls of the centrifuge. (The ram feed chamber was too small and only about a sixth of the mold surface could be covered with a full charge.)

The wet, loosely oriented-(hand) compressed mix was then centrifuged for one minute at low speeds (1000 rpm) to further orient and compress the mass. The centrifuge was stopped and an inner mandrel inserted. The inner mandrel used was an aluminum sheet 11-3/4" x 48" x 12 mils. The aluminum sheet was tightly rolled into a coil. The action of the centrifuge caused the coil to expand and exert fairly uniform pressure upon the glass flake mass. The centrifuge was run to top speeds (4000 rpm) for 15-20 minutes. The speed was then reduced to 1000 rpm and maintained until the resin B-staged (generally 20-35 minutes). The B-staged pipe was removed from the mold and fully cured in an oven.

A weighed amount of the 50/50 dry blended phenolic glass flake material was hand charged into the centrifuge. The centrifuge was started and xylene (solvent) was sprayed using an insecticide gun. The centrifuge was operated for one hour, after all the solvent was added, before it was stopped and glass wet-out observed. At 10%, 20%, and 50% solvent addition, based on total dry blend charged, the mass was only wet at the surface and was, therefore, essentially a loose dry blend. The mass was not self-supporting or tacky to the touch. Attempts to meter the glass resin and solvent spray by alternate addition of parts of the total charges were slightly more successful in producing a wet mass.



The wet Abbe premixed glass flake system was charged and packed into the slotted inner centrifuge chamber. The centrifuge was operated at the maximum speed until all the resin wet flakes had passed through the slots in the inner centrifuge core wall, Sketch 4. Residual wet glass flake resting between the rows of slots was then loosened from the inner wall by scraping with a spatula. The inner chamber was recharged and the cycle repeated until all the premixed resin required was added.

The centrifuge was then rotated at the 4000 rpm rate until the resin system had cured to a self-supporting state. The B-staged resin pipe was then removed from the mold and fully cured in an oven.

#### IV.3.4.6.1. Description of Centrifugal Cast Cylinders Produced

All the successfully prepared cylinders which have been produced were made with wet premixed systems. The attempts to produce cylinders using dry blended resin systems while not successful, did indicate that further development of this technique might yield a unique process. Table 40 lists all the cast sections which were prepared. The cylinders are 11-3/4" long and have an 8" O.D. and 6-1/2" I.D. and weigh as much as 9 pounds.

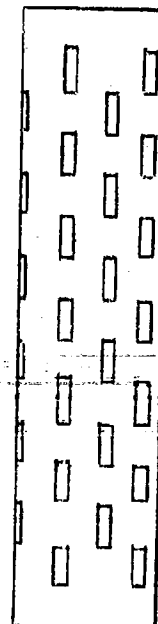
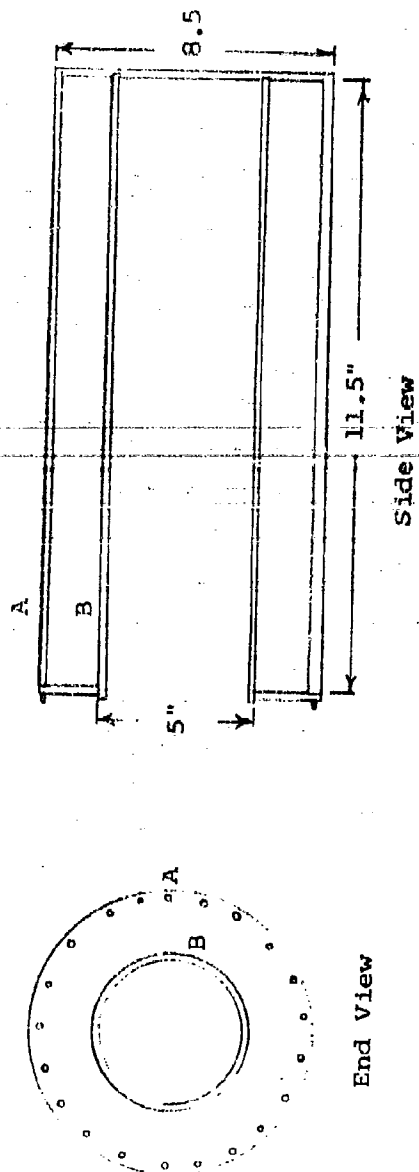
Cylinder #1 - The orientation of the flake in the pipe is good although some areas of flake disorientation are noticeable (Photograph 20). Attempts to cut one-inch rings from the end of the cylinder with a lathe cutter were unsuccessful; the 1" ring failed in areas of disorientation. The coiled aluminum sheet used as an inner molding mandrel surface was first tried in preparation of this unit. Previous moldings prepared without the aluminum mandrel resulted in poorly compressed weak castings. The inner surface of the cylinder has a pure polyester coating which cracked badly during the cure of the cylinder. Differential shrinkage rates of the glass flake layer and pure resin layer increased the size of the cracks to major proportions.

Cylinder #2 - The orientation of this unit is superior to cylinder #1 (Photograph 20). The areas of disoriented flake are not as noticeable. There is no excess resin layer present in this unit but the inner surface does not have a smooth finish like the outer surface (Photograph 22). One-inch rings were cut from this casting using the lathe cutter. Compressive strength and compressive hoop strength were determined.

Cylinder #3 - The complex shape shown in Photograph 21 was produced by building a plaster of Paris tapered ring in the center of the centrifuge chamber. The cast cylinder was removed from the centrifuge chamber with the plaster of Paris ring in place. The ring was broken to remove it from the cylinder.

Cylinder #4 - The plaster insert used to produce cylinder #3 was unsatisfactory and a metal tapered ring with flat land was machined. The ring was placed in the back of the mold before the charge was added to the centrifuge chamber. A one-inch strip of aluminum (12 mils thick) was inserted into the premix by hand.

Sketch A

Slotted Double Wall Centrifuge

Inner Centrifuge Core

Table 40

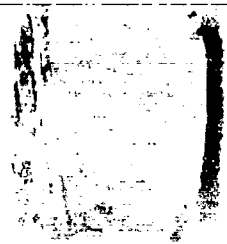
Centrifugal Cast Cylinder Data

<u>Cyl. No.</u>	<u>Resin</u>	<u>% Glass</u>	<u>Fabrication Method</u>	<u>Remarks</u>
1	Polyester	50	Hand Feed	Simple cylinder, coiled aluminum core used, excess resin inner layer
2	Epoxy	55	Hand Feed	Simple cylinder, coiled aluminum core used, no excess resin layer
3	Polyester	55	Hand Feed	Complex cylinder, plaster form and coiled aluminum core used, excess resin layer present
4	Polyester	60	Hand Feed	Complex shapes, steel form and coiled aluminum core used, resin dry and rich areas, spiral wound aluminum insert
5	Epoxy	55	Hand Feed	Complex shape (inner undercut and outer taper) no excess resin layer
6	Epoxy	55	Hand Feed	Complex shape (inner spiral groove and outer taper) no excess resin layer
7	Polyester	55	Double Wall	Simple cylinder, heavy resin layer split in two after curing
8	Epoxy	70	Double Wall	Incomplete casting, poor compression, non-continuous laminate
9	Epoxy	60	Double Wall	Dry appearing unit
10	Epoxy	60	Double Wall	Mandrel used, poor quality cylinder
11	Epoxy	50	Oriented Calendered Sheet	Excellent cylinder destroyed during cure

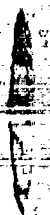
Table 40 (Continued)

<u>Cyl. No.</u>	<u>Resin</u>	<u>% Glass</u>	<u>Fabrication Method</u>	<u>Remarks</u>
12	Epoxy	50	Oriented Cal.	Excellent unit
13	Epoxy	60	1 ply wet cal. oriented sheet	Excellent part, collapsed during cure cycle
14	Epoxy	60	2 ply B-stage cal. oriented sheet	Excellent part, free of most visual defects
15	Epoxy	50	2 ply wet cal. oriented sheets	Mandrel used, very good orientation, excellent unit
16	Epoxy	50	Double Wall	Mandrel used, inner barrel slowed down, fair unit
17	Polyester	55	Double Wall	Mandrel used, inner barrel slowed down, excellent unit
18	Polyester	60	Double Wall	Mandrel used, inner barrel slowed down, excellent unit
Resin Formulations: Epoxy				
				(JD 509
				(Omamid C-288
				(Omamid T-590
Polyester				
				(Laminac 4128
				(Benzoyl Peroxide
				(Laminac Promoter 400

Photograph 20



Cylinder #3  
Polyester System



Cylinder #2  
Epoxy System  
Centrifugal Cast Cylinders  
Outside View



Cylinder #1  
Polyester System

Photograph 21



Centrifugal Cast Cylinder  
Cylinder #2  
Epoxy System  
Inside View

Photograph 22



Polyester System  
Metal Insert  
Cylinder #4

The strip was spirally coiled around the pipe circumventing the unit completely and touching both the inner and outer surfaces. The outer edge of the aluminum coil can be seen in Photograph 22. The inner surface of the cylinder had areas in which a pure resin layer was present and other areas which seemed to be resin-starved.

Cylinder #5 - A complex shape unit was produced by using the tapered ring to produce variation in outside dimensions and a removable inner ring to produce deviation in inside dimensions. The metal tapered ring was inserted and the charge added to the centrifuge. The coiled removable inner ring was then positioned. The aluminum inner mandrel was then inserted. The aluminum mandrel under centrifugal pressure forced the inner ring into the cylinder. Removal of the inner mandrel and inner ring from the cured casting resulted in an inner surface with an undercut with sharp sides circumventing the casting (Photographs 23, 24).

Cylinder #6 - Cylinder #6 was produced using the technique established in preparing cylinder #5, except for the form of the inner mold surface. To produce a deep, small cross-section undercut spiral groove in the inside surface, a simple rubber tube was spirally wound around the aluminum inner mandrel before it was inserted into the centrifuge chamber.

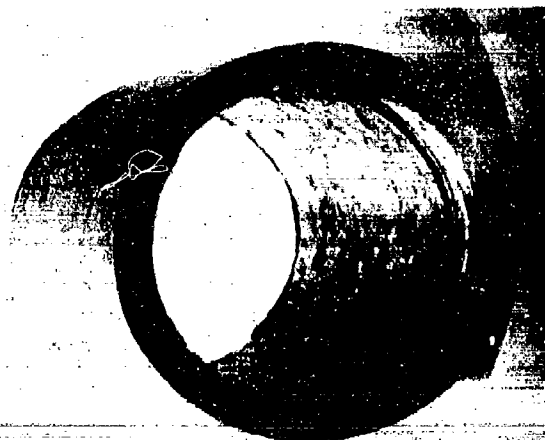
Cylinder #7 - The slotted double wall centrifuge (Photograph 25) assembly was used to produce this unit. The polyester system flowed from the inner core to the outer shell easily. The part produced contained a resin-rich to pure-resin inner surface. The part itself contained knit lines running the length of the cylinder. The knit lines corresponded to the rows of slotted openings in the inner core. The part was oriented between the knit lines but not in the knit line interface. The cylinder split along two of the knit lines (Photographs 26 and 27). The split is believed to have been caused by the constrictive pressure exerted on the cylinder by the relatively large amount of shrinkage of the inner layer of pure resin with respect to the resin-flake mixture. Examination of the unit showed the presence of deformation of the part's shape due to the resin shrinkage.

We believed that the knit lines could be eliminated by causing the inner core to rotate at a slightly lower rpm rate than the outer (mold) shell. The difference in rpm rates should cause the flake to be evenly distributed and deposited on the mold surface. Improvement in slot design would also be expected to eliminate orientation problems found at knit lines.

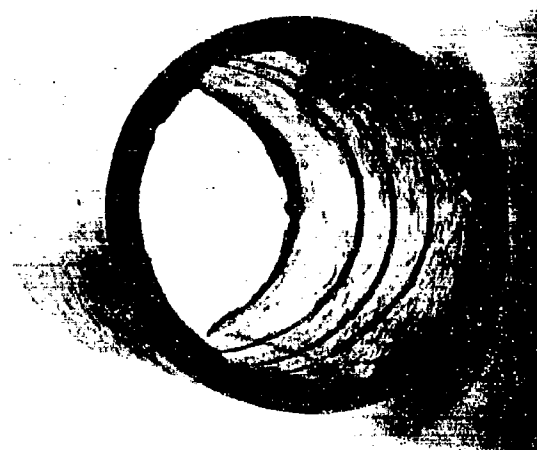
Cylinder #8 - The 70/30 flake epoxy system did not flow easily. A large portion (54%) of the batch was not used because the feed rate was too low. The material began to exotherm and had to be removed from the inner core before it "set up". The cast cylinder itself was loosely oriented and uncompressed and had an uneven inner surface with depressions running along the knit line area (Photograph 28).



Photograph 23



Cylinder #5



Cylinder #6

Cast Cylinders  
Inside View

Photograph 24



Cylinder #6



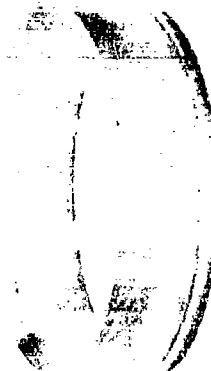
Cylinder #5

Cast Cylinders

Photograph 25



Slotted Double Wall  
Centrifuge  
(Inner Wall)



Tapered Inner Ring

Centrifuge Accessories

Photograph 26



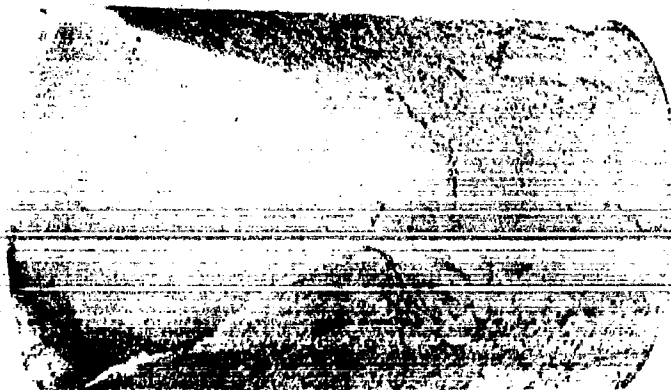
Cast Cylinder #7  
Outside View

Photograph 27



Cast Cylinder #7 - Split  
Inside View

Photograph 28



Cast Cylinder #8

Cylinder #8 - The slotted inner chamber was used to prepare this unit (60/40 glass to epoxy system). The rpm ratio of the inner core was lower than the mold chamber rpm rate. The rpm differential reduced the severity of the knit lines present in the inner surface of the molded unit. The positioning of the knit lines was not uniform as noticed in previously prepared units cast using the slotted centrifuge. An uneven thickness of glass flake resin was deposited on the mold surface, the back end of the casting was appreciably thicker than the forward-feed section. The outer surface was relatively smooth with no visible knit lines or major areas of dis-oriented flakes. The mass is relatively dry and does not have the outer resin coated appearance other specimens prepared with similar resin systems and ratios have.

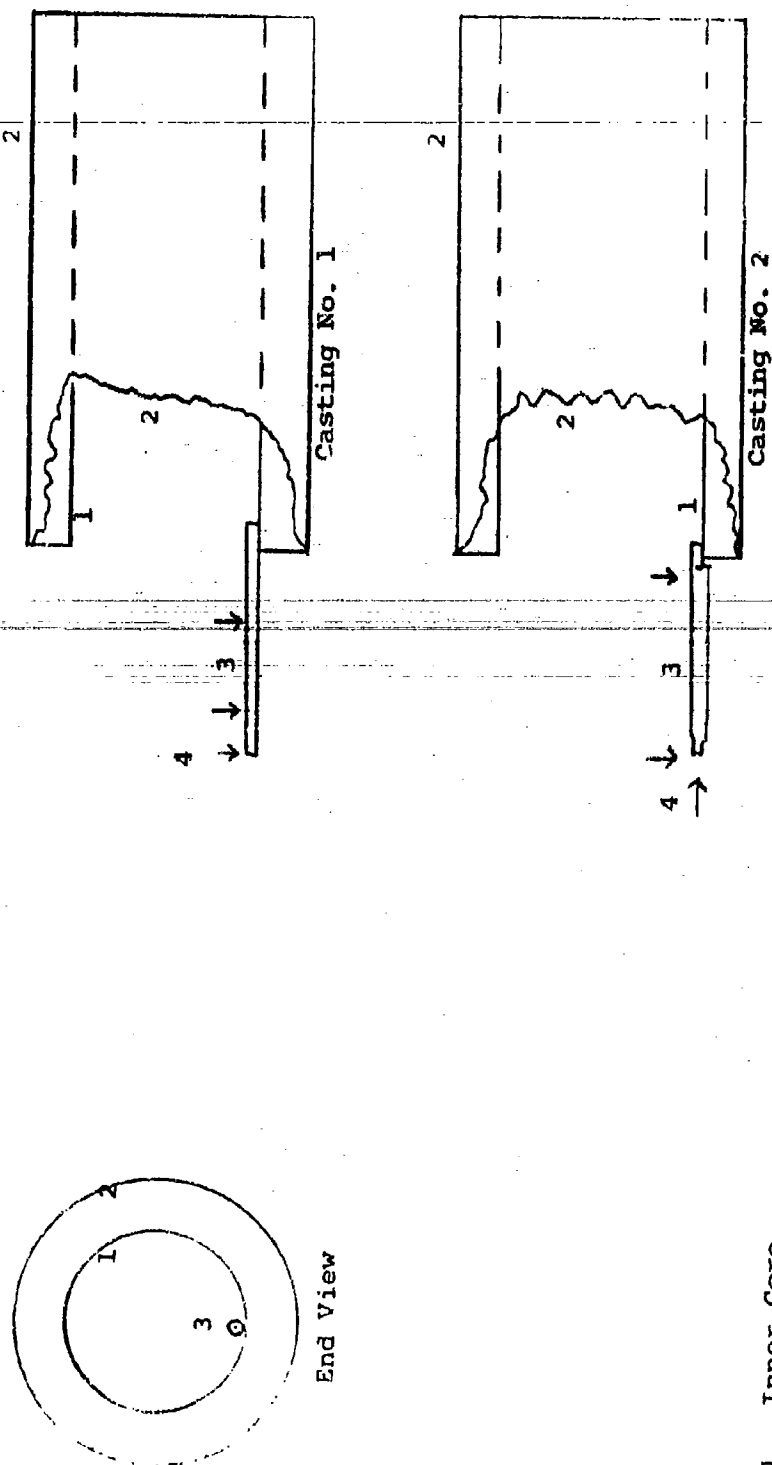
The reduction in inner core rpm rates was achieved by the crude mechanism of applying a drag on the freely rotating inner core. The drag was produced by applying pressure on the inner core by pressing an aluminum rod on the inner surface of the core. Sketch 5 shows the positioning of the drag rod in the assembly.

Cylinder #10 - The 60/40 resin system used was identical with cast cylinder #9. The slotted inner core was packed with the wet, loose, bulky glass flake and the centrifuge turned on. The glass flake passed from the inner core to the mold surface with some difficulty. When all the glass flakes were deposited, the inner core was removed and the inner expandable aluminum mandrel inserted in the mold. The charge used was small and uneven deposition in the mold chamber was encountered. Therefore, although the knit lines were greatly reduced and smooth areas were found in the inner area, the pipe was still poor in quality.

The results obtained from the above molding indicate a high potential for the system which is expected to permit centrifugal casting of complex shapes. The many drawbacks encountered are mechanical and may be corrected by modification in design of the slotted chamber and installation of proper mechanisms for control of rpm rates of the inner core.

Cylinder #11 - was prepared with oriented roller calendered sheet material. The wet 50/50 glass epoxy blend was calendered and a sample cut to predetermined dimensions from the wet sheet. The parting paper was then removed from the first and last 2 inches of the wet sheet material. The flexible wet casting was wrapped around the expandable aluminum mandrel and inserted in the mold. The centrifuge was rotated until the resin B-staged to a solid mass. The molding was removed from the mold the next morning and was put aside for 24 hours. After this long ambient cure cycle, the cylinder was placed in an oven heated to 120°F. to start the full cure cycle. After 10 minutes at this temperature, the section collapsed. Apparently, the temperature exceeded heat distortion point of the resin.

Before being placed in the oven, the cylinder was visually examined. The glass flake orientation was uniform; no flow lines, or faults were visible. The thickness of the unit was irregular due to the uneven thickness of the calendered sheet. There were several small entrapped air bubbles present in the cylinder.

SKETCH 4Slotted Double Wall Centrifuge

1. Inner Core
2. Outer Mold
3. Pressure Rod
4. Direction of Pressure Applied



Cylinder #12 was prepared from the same batch of calendered sheet material used to prepare cast cylinder #11, except that before centrifugal molding, the resin was permitted to B-stage overnight. The B-stage calendered, rigid and brittle sheet was cut to the correct size and heated in oven at 150°F. for 30 seconds to soften the sheet to a drapable sheet. The sheet was then wrapped around the aluminum core, inserted in the mold and cast. A hot air blower was placed at the front of the open mold and hot (150°F.) air was directed on the rotating cylinder for 30 minutes. The casting was 72 hours at room temperature; the unit was subjected to a curing schedule of 12 hours at 100°F., 12 hours at 125°F., 12 hours at 150°F., 12 hours at 200°F. and one hour at 300°F.

The molded cylinder has a visible lap joint, but is free of all visible flaws, voids and orientation defects, is uneven in thickness due to defects in the roller orientation mechanism and has several small air bubbles entrapped in the material.

Cylinder #13 - Two plies of roller-calendered premix sheet were wrapped around the expandable aluminum mandrel. The B-staged unit was destroyed during the cure cycle. The 100°F. cure temperature exceeded the heat distortion point of the B-staged resin.

Cylinder #14 - Two plies of B-staged roller-calendered premix were used. The unit was centrifuged and cured. An excellent part was obtained free from most visual defects.

Cylinder #15 - Two plies of wet roller calender sheet were wrapped around the aluminum mandrel. The unit was cured and examined. Knit lines are not visible and most laminate defects were not present. The laminate does have one molded line present which was caused by a fold in the parting paper.

Cylinder #16 - The slotted centrifuge inner chamber was used to prepare this part. Knit line disorientation was reduced and now seems to be caused by an overlap or sheet joining difficulty.

Cylinder #17 - The slotted centrifuge inner chamber was used to produce this polyester based cylinder. The 55% glass content is sufficiently low to permit formation of thin resin rich areas on the inside of the pipe which cracked during the cure cycle. The inner mandrel was used for this molding (Photograph 29).

Cylinder #18 - The slotted centrifuge inner chamber was used to produce this 60% glass content cylinder. The inner expandable mandrel was used and the rpm was reduced sufficiently to result in a reduction of knit lines in the cylinder (Photograph 30).

#### IV.3.4.6.2. Conclusions

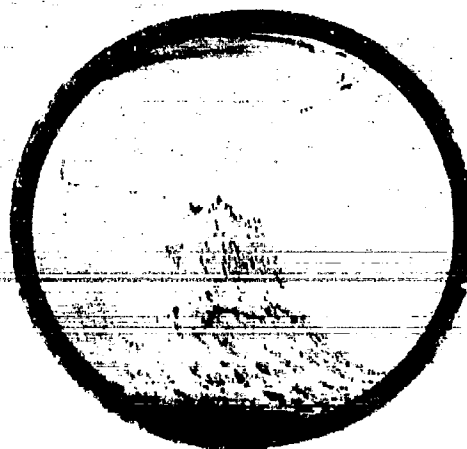
Several simple and complex shaped cylinders have been produced using the 4000 rpm horizontal centrifugal casting apparatus and room temperature curing epoxy and polyester wet premix systems. The complex shaped pipes have variations in inside and outside diameters.

Photograph 29



Cast Cylinder #7

Photograph 30



Cast Cylinder #18

One cylinder contains a metallic aluminum insert in the form of a spirally coiled ribbon circumfused in the matrix and touching both inner and outer surfaces. The wet blended systems were premixed in the Abbe mixer in 50/50, 55/45, 60/40 and 70/30 glass flake to resin ratios.

All successful moldings were prepared from wet premix systems. Attempts to centrifugally cast pipe from dry blended pulverized phenolic-glass flake mix were unsuccessful. We attempted to use this system to produce a cast pipe with maximum glass flake particle size. Dry blending of glass flake results in minor particle size degradation. Therefore, if dry blended glass resin blends could be centrifugally cast, particle size could be maintained at a maximum, which we believe would contribute significantly to the ultimate strength of the laminate.

Several laminates have been produced using a double-walled centrifuge technique. Attempts were made to determine if an inner centrifuge chamber which has multiple openings in the surface could be used to meter, orient, and produce complex shapes. The simple pipe inner core demonstrated that premixed wet resin glass flake systems exhibited sufficient flow to permit passage from the inner chamber to the outer molding chamber.

#### IV.3.5. Effect of Processing Upon Glass Flakes

##### IV.3.5.1. Introduction

Commercial glass flake is produced by blowing large diameter tubes or bubbles having a wall thickness of 2 microns from molten E glass tubing and then crushing the cooled and solidified film to produce flakes. The process produces a variety of flake shapes and sizes. The flakes have irregular notch edges, varied diameters and a slight curvature. No attempt is made to classify commercial flake into flake diameter ranges. Therefore, commercial flake contains a range of materials, from a fine dust up to individual flakes 1/2 inch in length. During the course of the glass flake study, appreciable differences in the appearance were noted when large bulks of flakes were viewed.

The degree and extent of variation in glass flake size distributions in commercial glass flake were believed to be contributing to difficulty in obtaining laminates having high strength. The relationship between original glass flake size distribution and glass flake breakdown during processing and molding and its eventual effect upon laminate physical properties were studied intensively.

##### IV.3.5.2. Analysis of Commercial Glass Flakes

A determination of the variation in the size distribution in seven unopened boxes of glass flake is presented in Table 41. In addition, size distribution of five other boxes are listed. The last five batches were evaluated as part of other phases of the contract. Examination of Table 41 shows major variations in commercial glass flake size distribution do exist.

TABLE 11

Variation in Size Distribution of Commercial Flake

Sample (Box) Identification	Screen Mesh Size						% Pan	% Loss
	% +4	% +8	% +16	% +30	% +50	% +100		
A*	8.7	42.1	33.5	8.7	5.8	0.6	0.3	0.3
B	11.4	43.3	27.9	8.1	5.2	1.7	0.7	1.7
C	65.8	12.3	12.6	3.8	3.2	1.2	0.4	0.7
D	13.5	49.1	21.6	6.8	5.0	1.8	0.7	1.5
E	12.7	40.9	29.2	7.7	5.8	2.1	0.5	1.1
F	14.7	45.9	23.9	7.3	4.9	1.7	0.7	0.9
G	11.9	45.3	28.7	5.4	5.2	1.7	0.6	1.2
1**	71.0	15.1	6.9	1.9	1.1	1.1	0.8	2.1
2	-	73.6	11.5	5.1	6.0	2.9	2.0	2.0
3	70.7	14.6	8.5	1.8	1.3	0.5	0.4	2.1
4	54.2	20.4	11.0	3.4	4.6	1.7	1.7	1.3
5	-	52.5	23.5	14.0	7.0	3.0	trace	0

\*Boxes A-G on Hand

\*\* Material processed and data collected from previous studies

All identification and markings on boxes A through G are identical, however, no identification as to lot number was present. Therefore, we cannot judge if the measured differences in size distribution could be attributed to lot variation or to other variables of manufacture, handling, storage or transport.

Box C contains the highest percentage of flakes having greater than 4 mesh size. This difference was detectable visually.

#### IV.3.5.3. Glass Breakdown Study - Abbe Mixing

From early glass flake degradation studies performed in other phases of the contract, it was established that the larger glass flakes disappeared rapidly during the blending operations. The preliminary studies were performed with glass flake to resin ratios of 50/50 up to 70/30. This study (Table 42) was performed with uncatalyzed resin in a 60/40 resin to glass flake ratio. The high resin content was used to reduce the excessive degradation rate experienced at higher glass flake ratios. It was already known that as the resin content was decreased, the degradation rate increased. Uncatalyzed resin was used to permit ease of clean up and to prevent resin cure during the long mixing cycle (one hour) investigated.

Three different boxes of glass flake were used (B, C & G) in the study. Boxes B and G have almost identical original glass flake size distribution. Box C has a completely different glass flake distribution composition.

The study was designed to determine if glass flake with similar initial glass flake size distribution would degrade at the same rate during processing. It was also designed to determine if a batch of glass flakes with a higher percentage of larger original glass flakes would effect the glass flake size distribution of the final premixed system.

From our experience we believed that batches of glass flake degraded at different rates as a result of variation in internal stress concentrations in individual glass flakes, faults, cracks, and jagged edges introduced through the glass flake production technique.

Flake glass was slowly added to the resin in the Abbe mixer over a 15 minute period of time. The Abbe mixer blades were rotating the lowest speed 12/6 rpm during the glass flake addition. After all the flake was added, the blade rpm was increased to 100/50 rpm. Ten minutes after all the glass flake was added, a sample of premix was removed from the ball on the slower moving blade. Additional samples were removed from the mixer at 10 minute intervals and flake glass size distribution of the samples was determined.

#### IV.3.5.3.1. Method of Determining Glass Flake Size Distribution

The glass flake distribution of all samples were determined using the techniques outlined below:

TABLE 42

## GLASS BREAKDOWN STUDY

Effect of Original Glass Flake Size Distribution  
Upon the Rate in Flake Size Degradation During Mixing

Sample (Box) Identification	% +4	% +8	% +16	% +30	% +50	% +100	% Pan	% Loss	% Glass
B Unmixed	11.4	43.3	27.9	8.1	5.2	1.7	0.7	1.7	100
10 min. mixing	-	-	trace	2.2	43.6	30.6	22.4	1.2	41.7
20 min. mixing	-	-	trace	0.4	28.7	37.2	32.6	1.1	41.7
30 min. mixing	-	-	0.1	0.1	18.5	36.8	42.8	1.8	42.1
40 min. mixing	-	-	0.1	0.1	17.3	37.5	43.7	1.3	42.2
50 min. mixing	-	-	0.1	0.1	17.7	39.1	41.5	1.5	41.8
60 min. mixing	-	-	trace	0.1	17.1	39.9	41.5	1.4	42.2
G unmixed	11.9	45.3	28.7	5.4	5.2	1.7	0.6	1.2	100
10 min. mixing	-	-	trace	2.9	33.2	38.9	23.9	1.1	40.3
20 min. mixing	-	-	trace	0.9	26.0	40.2	31.8	1.1	40.0
30 min. mixing	-	-	trace	0.3	17.1	41.5	40.1	1.0	41.0
40 min. mixing	-	-	trace	0.2	16.4	41.8	40.6	1.0	
50 min. mixing	-	-	trace	0.1	14.2	42.7	42.1	0.9	
60 min. mixing	-	-	trace	0.1	10.4	42.1	46.8	0.6	
C unmixed	65.8	12.3	12.6	3.8	3.2	1.2	0.4	0.7	100
10 min. mixing	-	-	0.1	3.0	35.4	38.3	22.4	0.8	40.3
20 min. mixing	-	-	0.1	0.9	22.7	40.9	34.8	0.6	39.8
30 min. mixing	-	-	trace	0.3	17.3	44.2	37.1	1.1	39.8
40 min. mixing	-	-	trace	0.2	12.9	42.9	42.6	1.4	39.9
50 min. mixing	-	-	0.1	0.1	11.3	44.5	43.0	1.0	40.0
60 min. mixing	-	-	trace	0.1	9.2	45.1	45.0	0.6	39.8

Mixed 60% resin/40% Glass 15 minutes glass flake addition time  
Uncatalysed Epon 828 used.

a. Freshly Mixed and Uncured Resin-Glass Flake Mixtures

- (1) A weighed sample of the resin glass flake mixture is dissolved in acetone.
- (2) The sample is washed by decantation and filtration until filtrate shows no cloudiness in water.
- (3) The glass flake is dried on a funnel in an air-circulation oven for one hour.
- (4) The sample is cooled under suction with a water aspirator.
- (5) The glass flake recovered are weighed and the glass flake content calculated as a percentage of the total specimen weight.
- (6) The recovered glass flake is placed on an 8 mesh standard sieve which contains the under size series 16, 30, 50, and 100 mesh screens.
- (7) The screen assembly is placed on a Ro-Tax shaker for 10 minutes.
- (8) The glass flake on each screen and in the bottom pan are weighed.
- (9) The flake size distribution is calculated as percentage of the total flake composition.

b. Resin Glass Flake Mixtures that are Partially or Completely Cured

(Only partially soluble in acetone)

- (1) A weighed sample is digested in approximately five times the sample weight of concentrated nitric acid or about four times the sample weight in fuming nitric acid.
- (2) The mixture is heated until the resin in the mixture has been dissolved and only a trace of brown fumes is given off.
- (3) The acid mixture is washed with nitric acid by decantation and filtration until the filtrate shows no precipitate or discoloration in water.  
Note: Nitrated resins are soluble in concentrated nitric acid.
- (4) The recovered glass flake is washed with water until free of nitric acid. (Test with pH paper.)
- (5) The recovered glass flakes are washed with acetone to remove all water and all traces of resin.
- (6) The glass flakes are dried on the Buchner funnel in an air-circulation oven for one hour.  
Note: In some cases the glass flake will have a pale yellow color. Removing the last traces of organic nitric acid derivatives by heating in a furnace at 1100°F. for 3 hours did not change the recovered glass content by more than a few tenths of a per cent.
- (7) The percentage of glass content is calculated from the weight of the recovered glass.
- (8) Steps f, g, h, and i of procedure "A" are reported.



### c. General Considerations

For a simple glass flake content determination, one to five grams of sample are required. For a screen analysis, a minimum of 25 grams of sample is required to keep the losses of handling below 5%.

#### IV.3.5.3.2. Separation Equipment

An 18" diameter model of the Sweco Vibro-Screen Separator, Photograph 31, was used to classify the glass flake into +8, -8, +16, -16, +30, +50, +100, and -100 mesh fractions for particle size studies in glass flake. This separator classified the flake effectively without static charge inducement by causing the material to trace a spiral path across a screening surface and into a discharge chute. Fines fall through the screen and go through the same process until classified. The only disadvantage being that screening rates are very slow; feed must be restricted or it will cover the entire screen and not be classified. This was an expected inherent problem because of the flake volume to weight ratio.

The glass flake samples removed from the mixers and laminates were classified on a Rotap screen sieve assembly which is a more accurate device for laboratory investigations than the larger Sweco. The relatively small samples 25-50 grams were placed in the upper screen and the machine operated for 10 minutes. The weight of sample contained on each individual screen was determined and glass flake distribution calculated.

The data in Table 42 is presented in graphic form in Figures 6, 7 and 8. Examination of the data and graphs shows that the major portion of the glass flake breakdown occurs within the first 10 minutes of mixing. It should be noted that blending times for maximum flake wet out are on the order of 20 minutes.

The data has been arranged in Table 43 to compare the glass flake size distribution of three blends. The data is also presented in graphic form in Figures 9, 10, 11, 12, 13, 14 and 15. Figure 9 shows the original dissimilarity in glass flake size distribution between Box C and Boxes B and G. It also shows how similar Boxes B and G were originally in size distribution. The data in Figure 10 shows that after only 10 minutes of mixing, the +16 mesh and higher glass flakes have virtually disappeared from the blend. It also shows that glass from Box C actually degraded at a faster rate than the glass in Boxes B and G, and further, after mixing, the amount of large flake present was insignificant. Figure 11 shows that after 20 minutes of mixing, all +16 mesh glass flakes had disappeared from glass taken from Boxes B and G and that less than 1% glass remained on the +30 mesh screen.

Figures 12-15 show that the glass flakes breakdown does vary from lot to lot but more importantly it shows that less than 20% of the glass flake is retained on a +50 mesh screen. A 50 mesh screen has openings of 0.0117 inches; the 30 mesh screen has openings of 0.0232 inches. Therefore, over eighty per cent of the glass in the

Photograph 31



Sweco Vibro Screen Separator

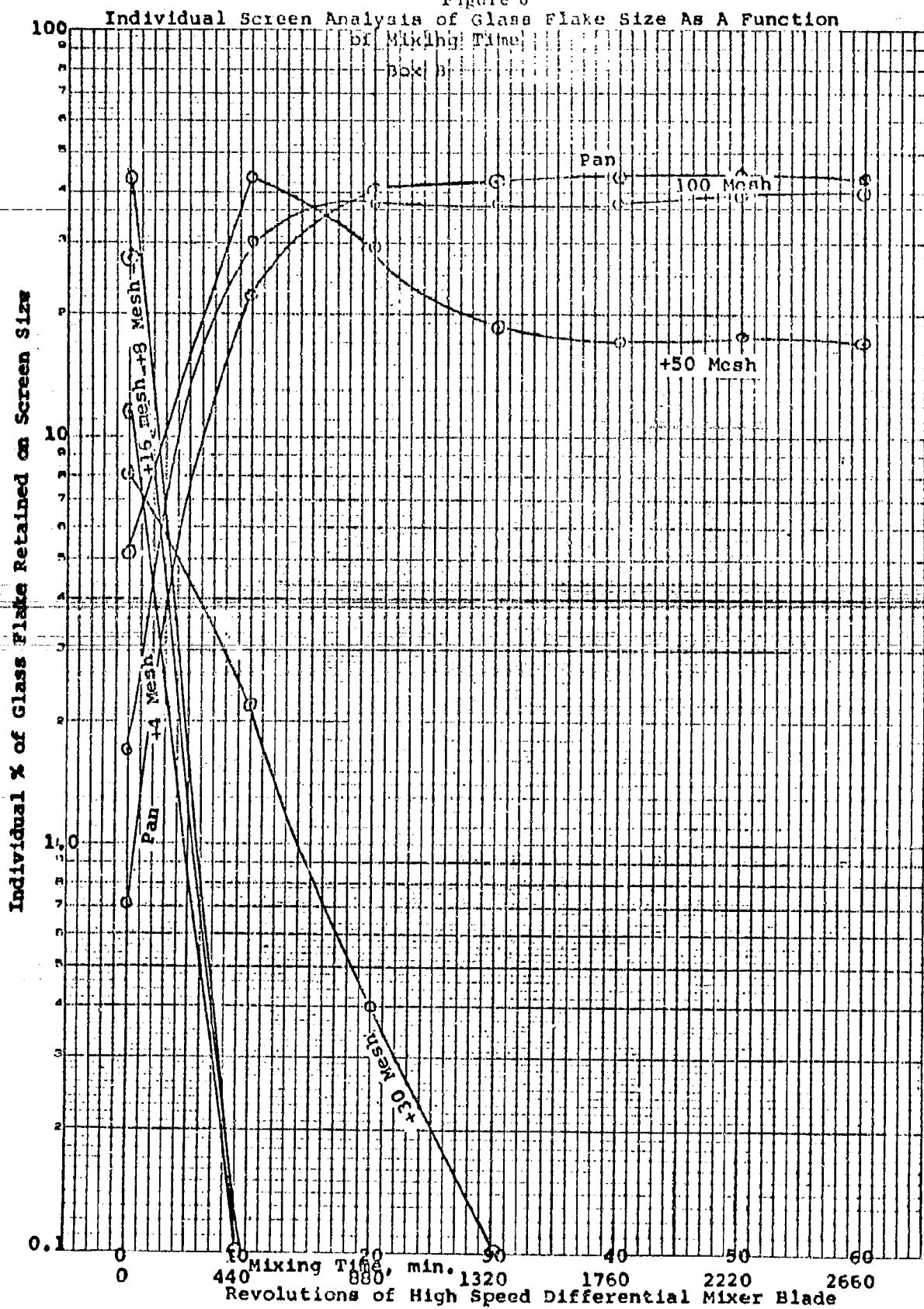


Figure 7

Individual Screen Analysis of Glass Flake Size As A

151.

Function of Mixing Time

Box C

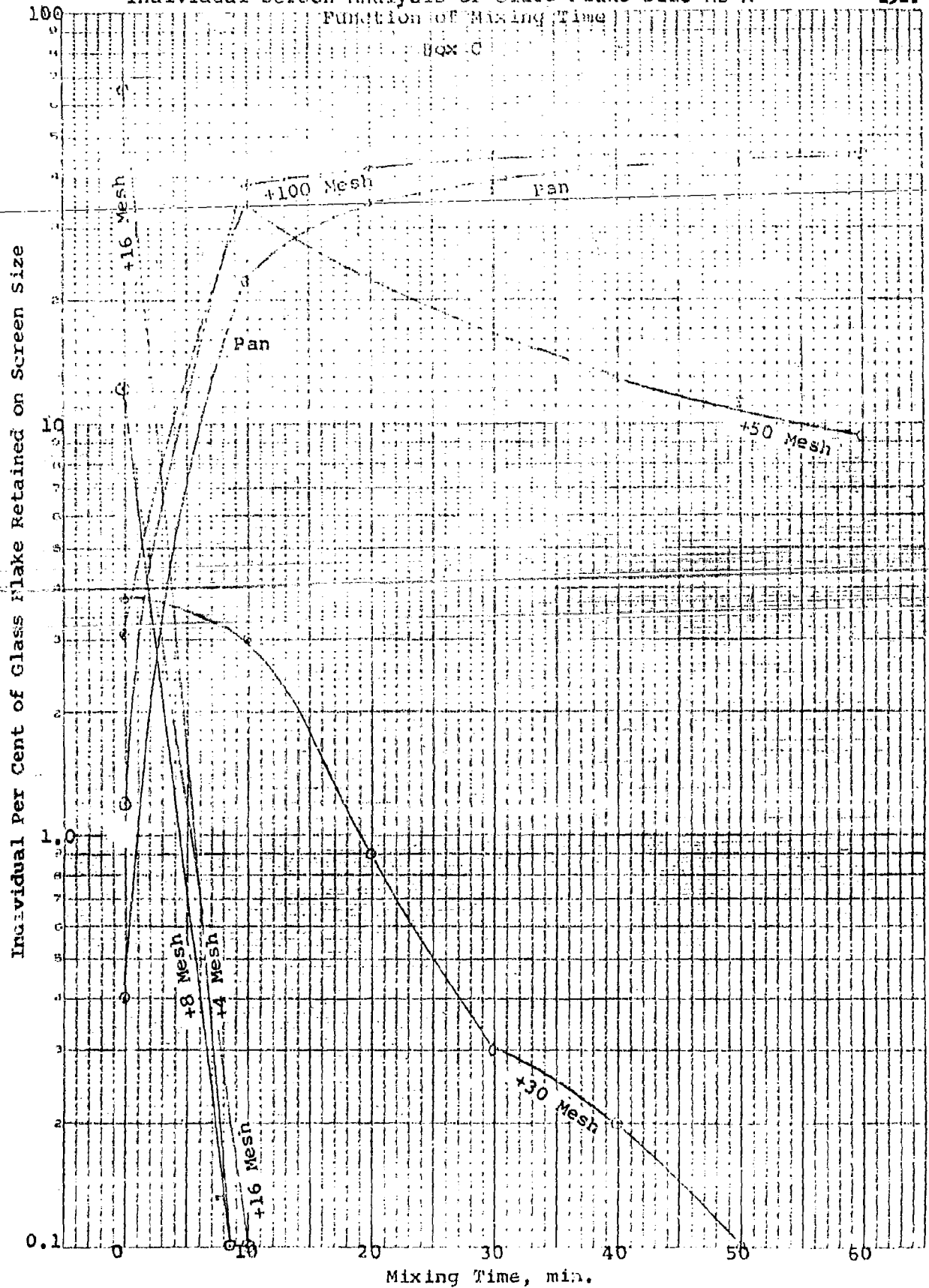


Figure 8  
Individual Screen Analysis of Glass Flake Size as a  
Function of Mixing Time:

152.

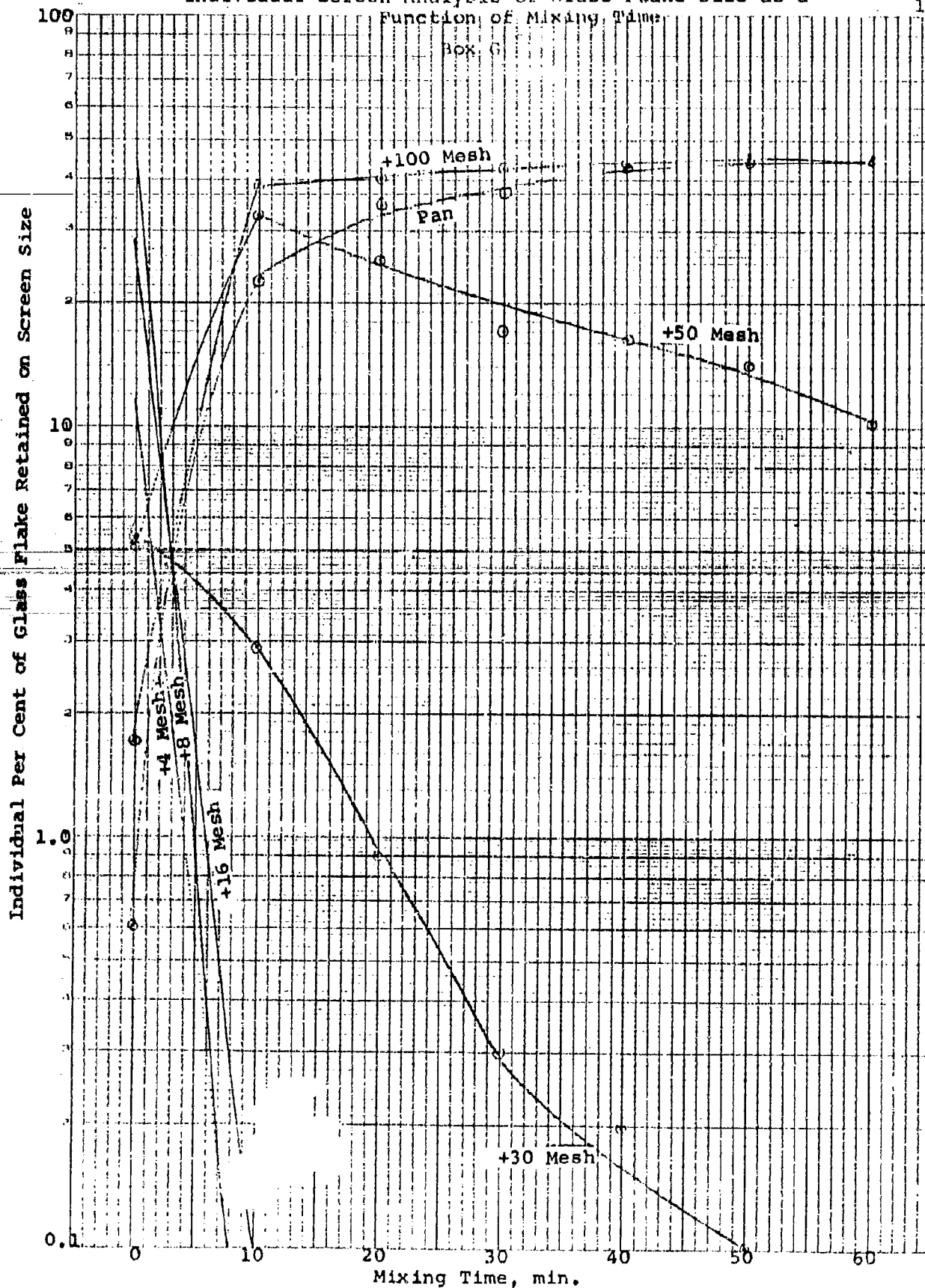


TABLE 43

Glass Break Down StudyComparison of Glass Break Down Resulting From Variations in Original Glass Flake Size

Sample (Box) Identification	Screen Mesh Size					% Pan	% Loss	% Glass
	% +4	% +8	% +16	% +30	% +50			
Unmixed								
B	11.4	43.3	27.9	8.1	5.2	0.7	1.7	100
G	11.9	45.3	28.7	5.4	5.2	0.6	1.2	100
C	65.8	12.3	12.6	8.8	3.2	0.4	0.7	100
10 Minute Mixing								
B	-	-	trace	2.2	43.6	22.4	1.2	41.7
G	-	-	trace	2.9	33.2	23.9	1.1	40.3
C	-	-	0.1	3.0	35.4	22.4	0.8	40.3
20 Minute Mixing								
B	-	-	trace	0.4	28.7	32.6	1.1	41.7
G	-	-	trace	0.9	26.0	31.8	1.1	40.3
C	-	-	0.1	0.9	22.7	34.8	0.6	39.8
30 Minute Mixing								
B	-	-	0.1	0.1	18.5	42.8	1.8	42.1
G	-	-	trace	0.3	17.1	40.1	1.0	41.0
C	-	-	trace	0.3	17.3	37.1	1.1	39.8
40 Minute Mixing								
B	-	-	0.1	0.1	17.3	43.7	1.3	42.2
G	-	-	trace	0.2	16.4	40.6	1.0	40.5
C	-	-	trace	0.2	12.9	42.6	1.4	39.9
50 Minute Mixing								
B	-	-	0.1	0.1	17.7	41.5	1.5	41.8
G	-	-	trace	0.1	14.2	42.1	0.9	40.3
C	-	-	0.1	0.1	11.3	43.0	1.0	40.0
60 Minute Mixing								
B	-	-	trace	0.1	17.1	41.5	1.4	42.2
G	-	-	trace	0.1	10.4	46.8	0.6	40.3
C	-	-	trace	0.1	9.2	45.0	0.6	39.6

Figure 9

## Comparison of Size Degradation of Different Lots of Glass Flake

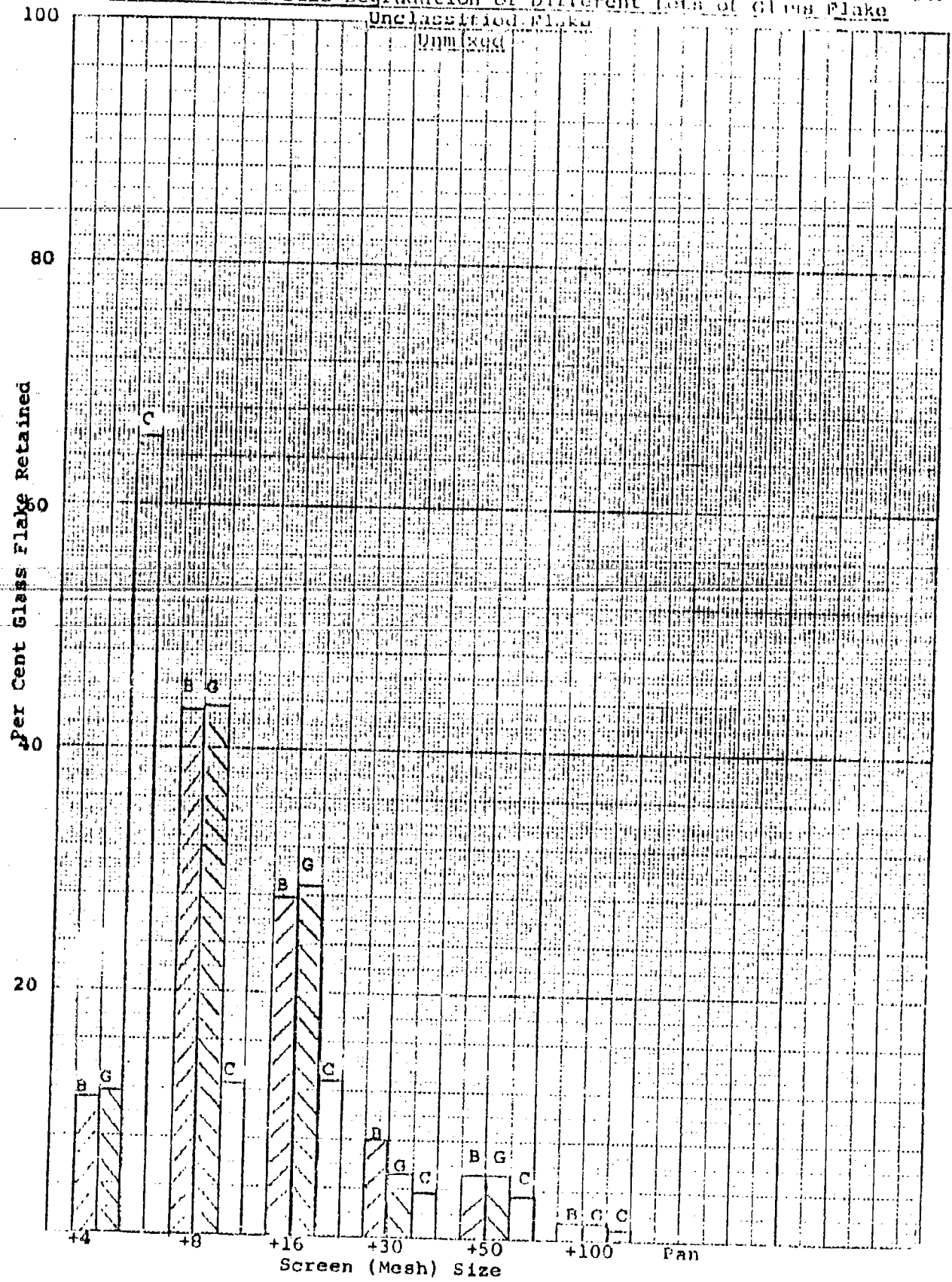


Figure 10  
Comparison of Size Degradation of Different Lots of Glass Flake

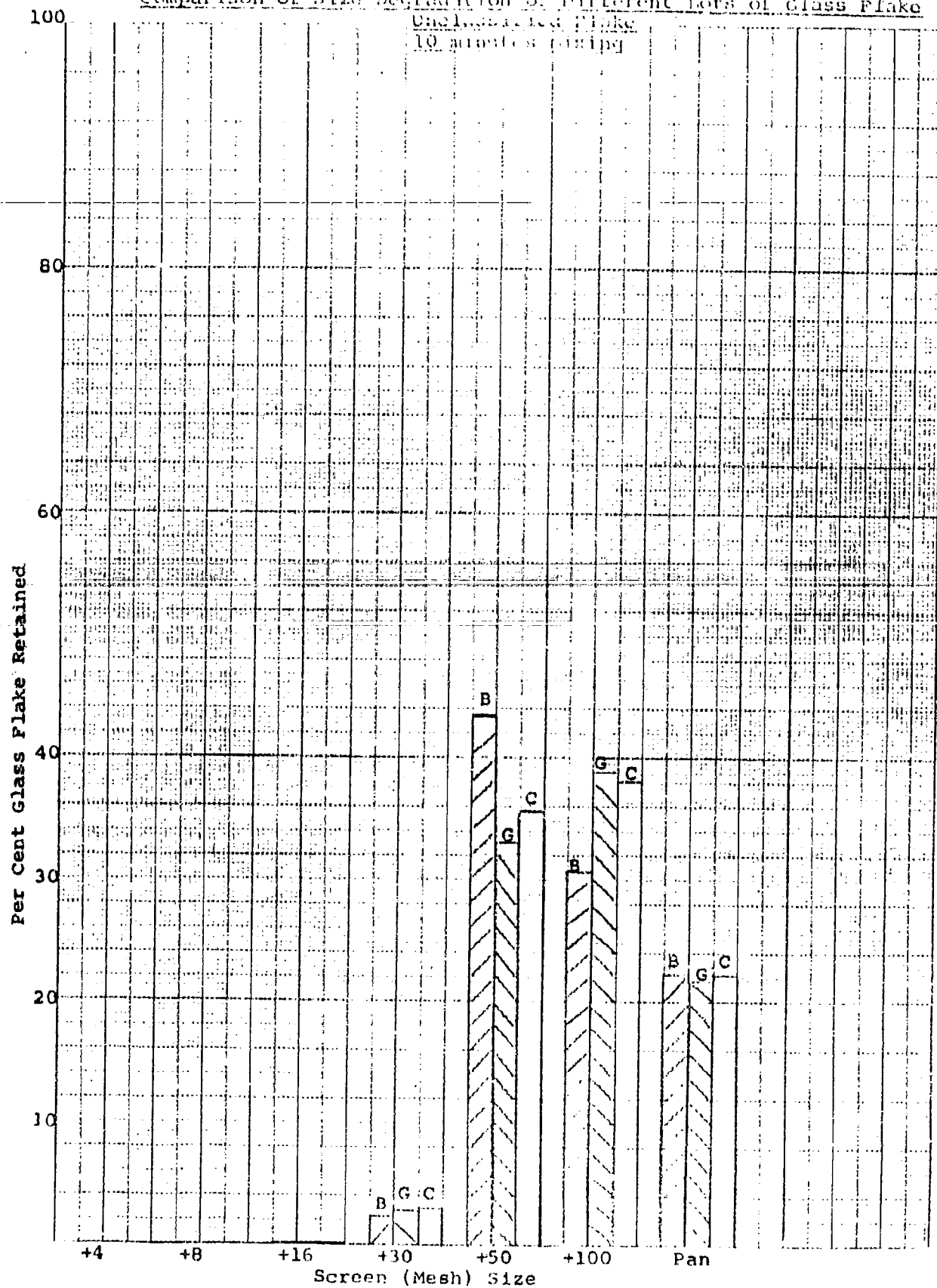
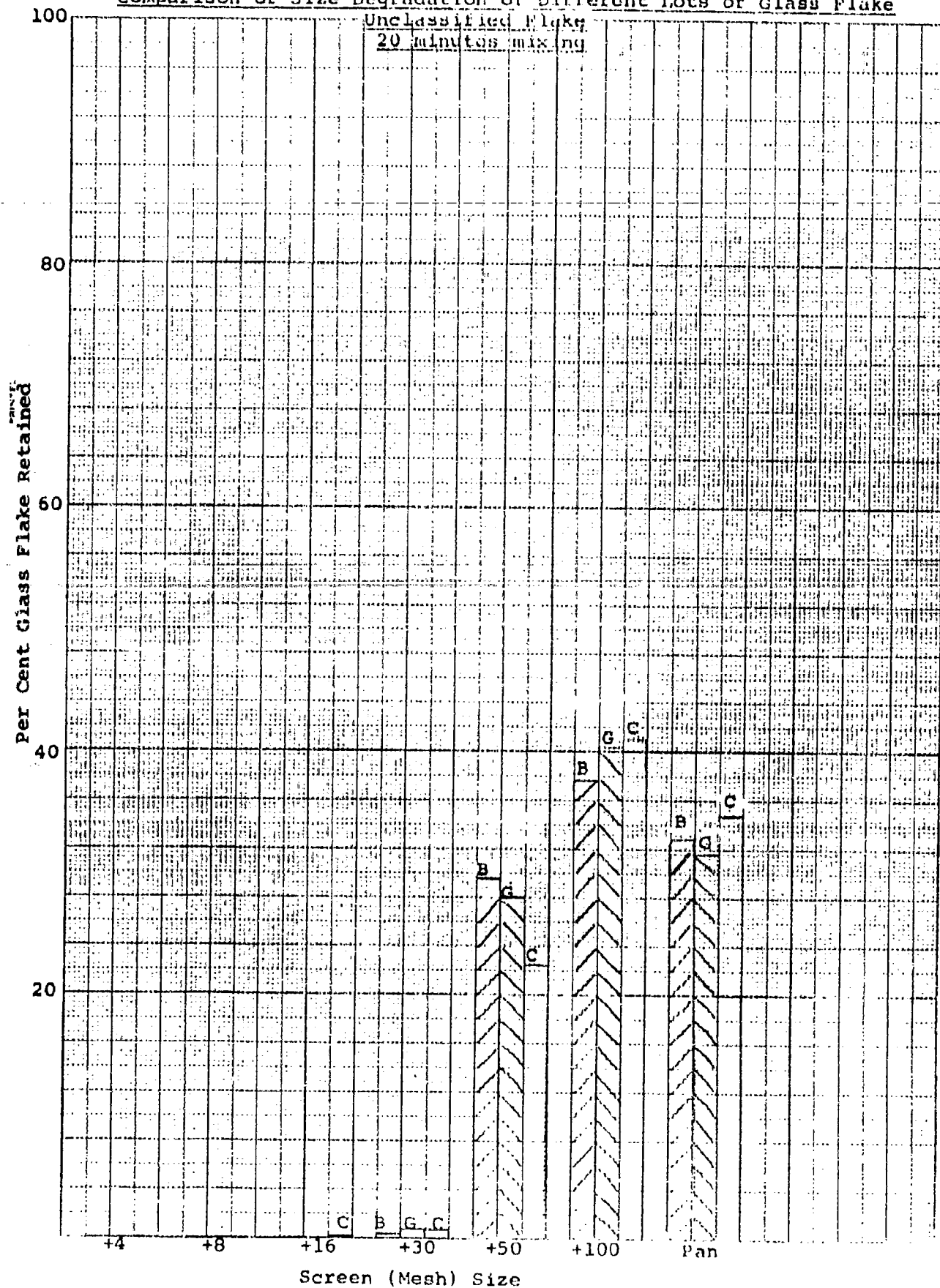




Figure 11

## Comparison of Size Degradation of Different Lots of Glass Flake



## Comparison of Size Degradation of Different Lots of Glass Flake

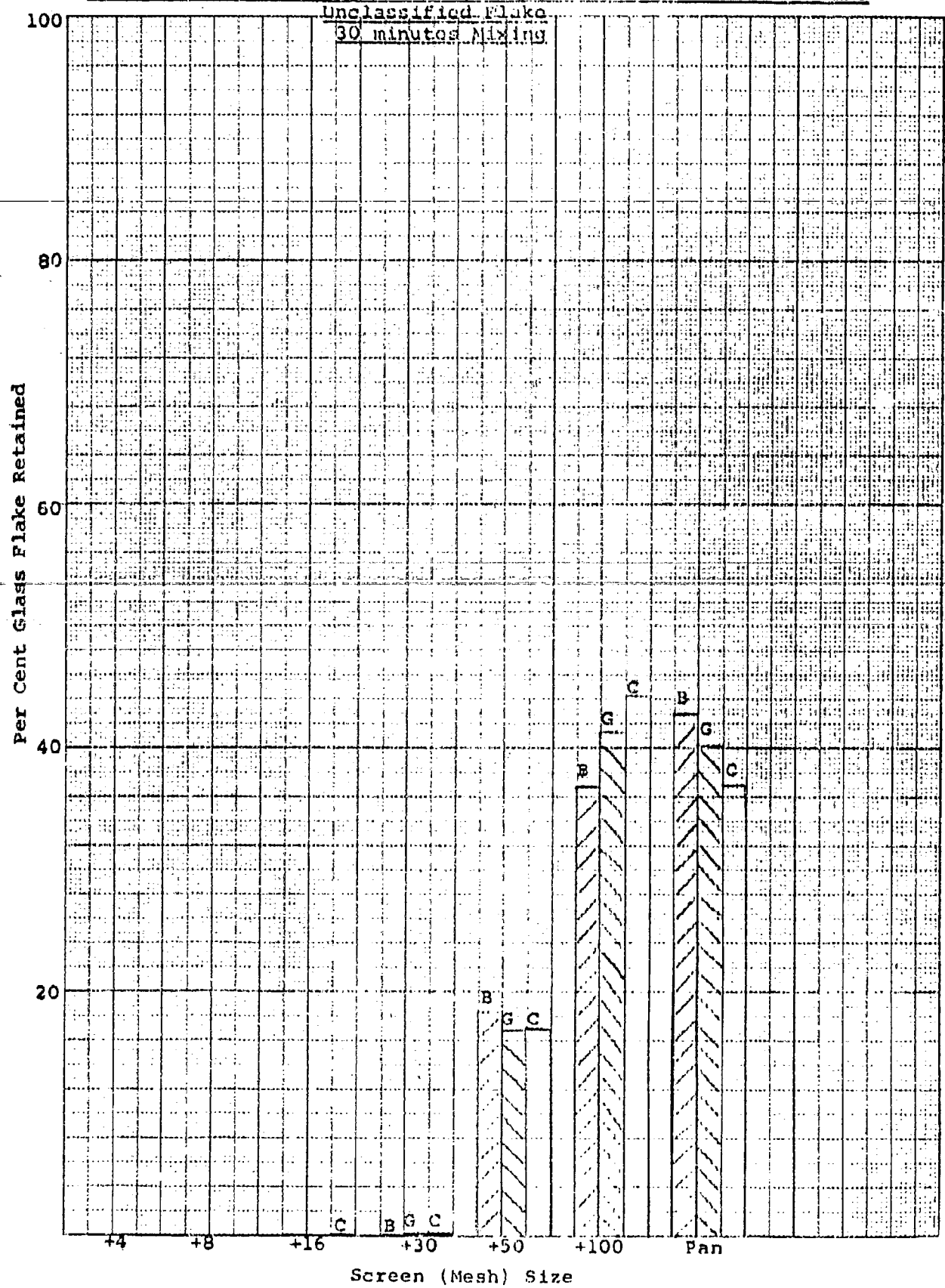


Figure 13

Comparison of Size Degradation of Different Lots of Glass Flake 158.

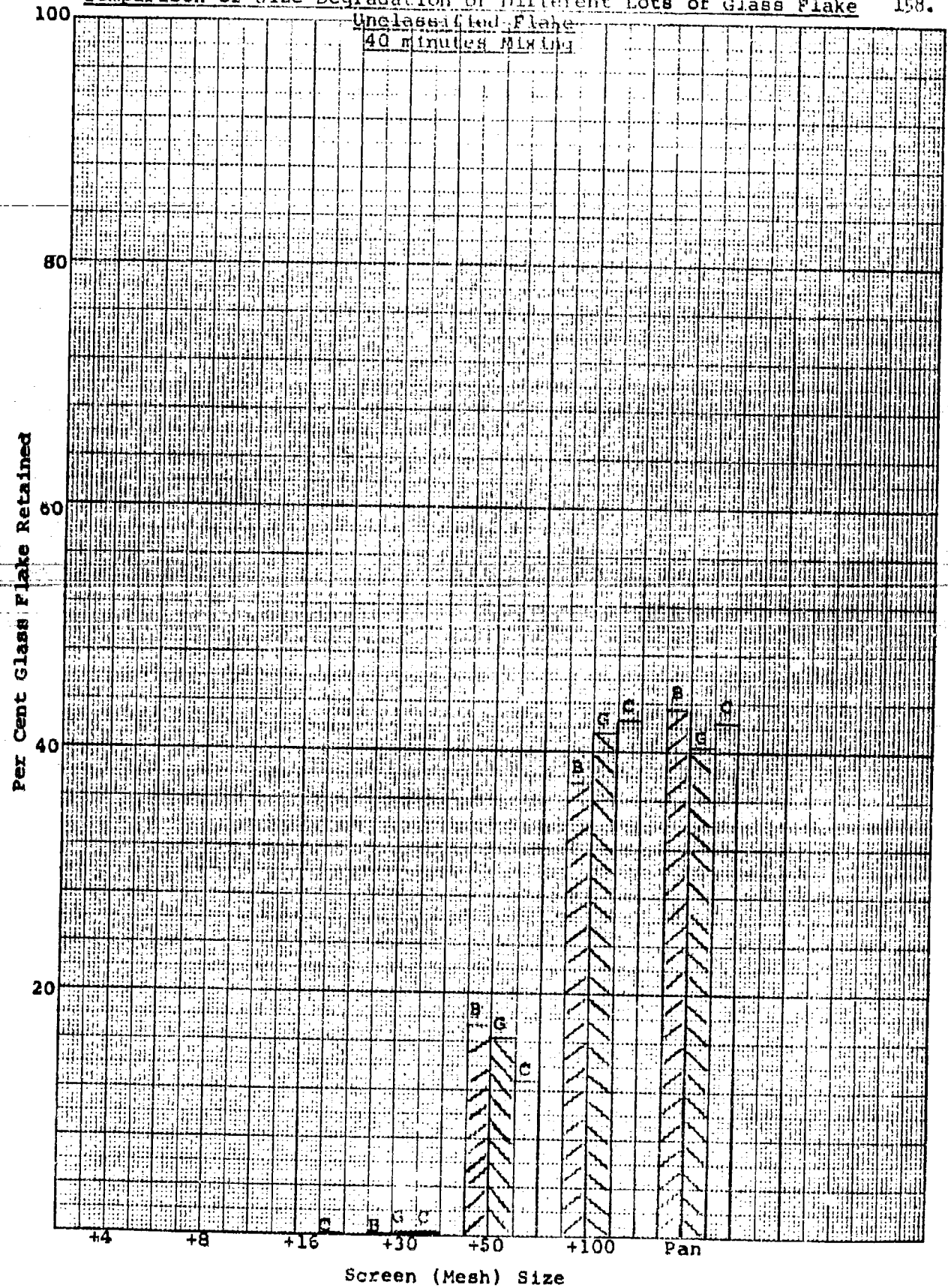
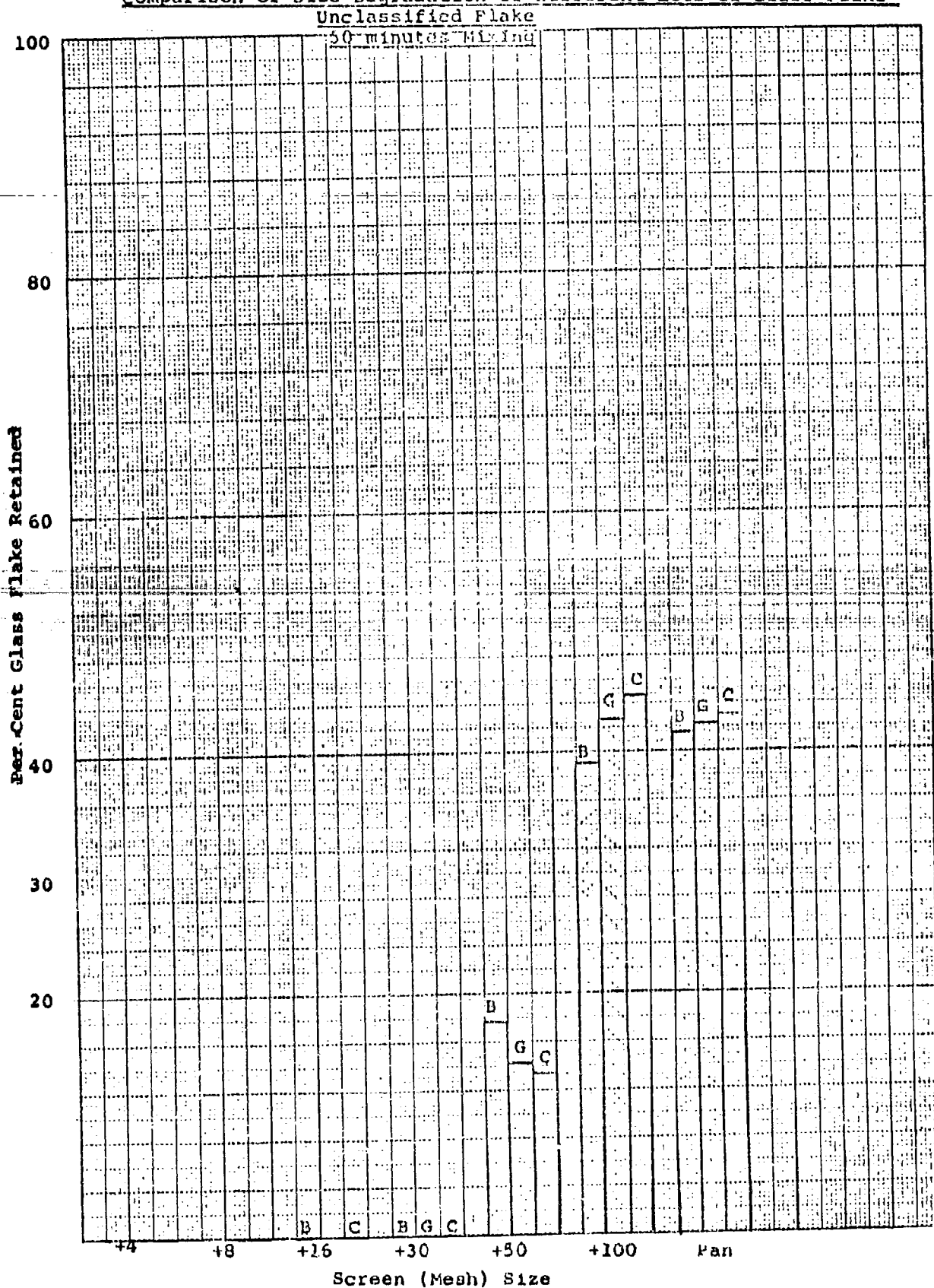
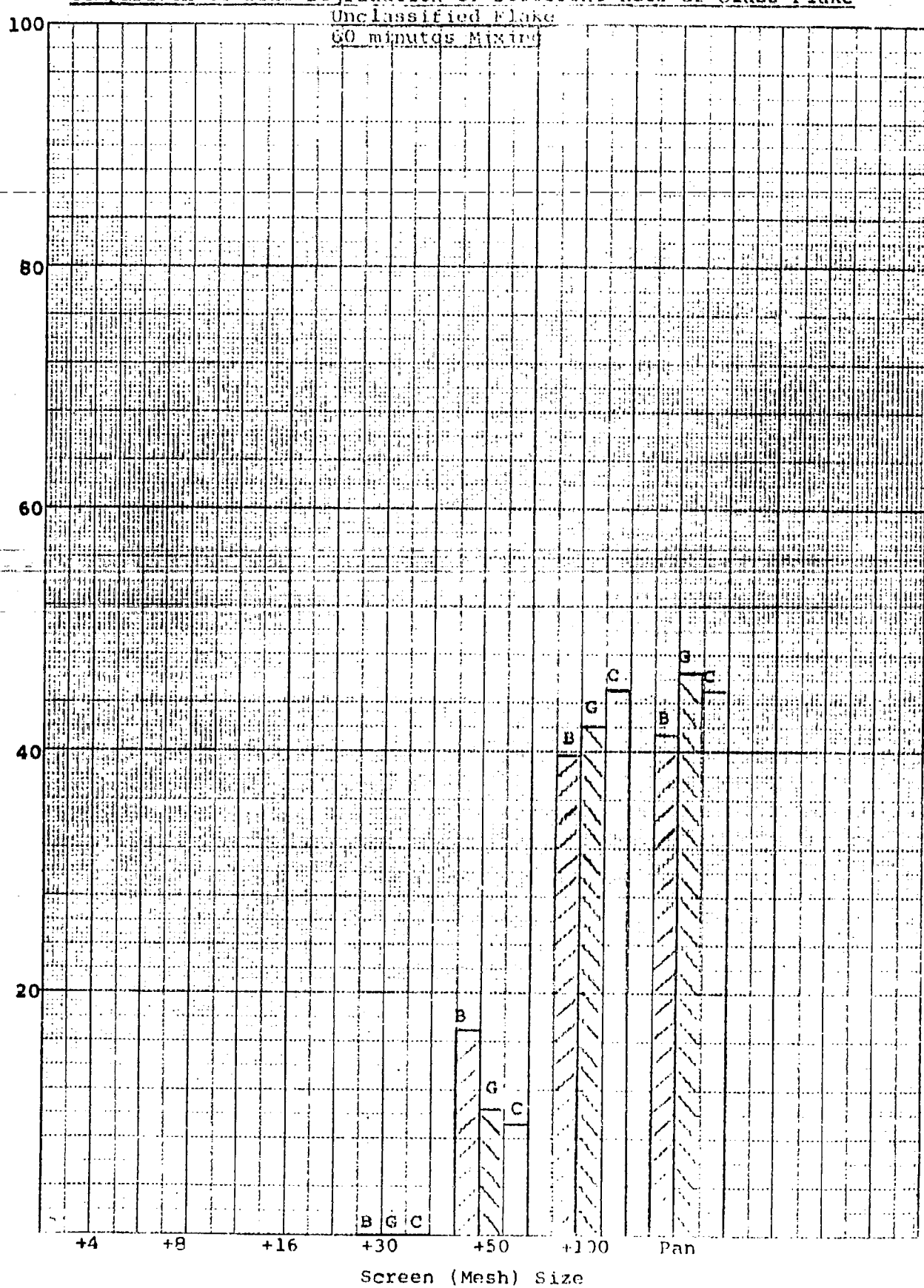


Figure 14  
Comparison of Size Degradation of Different Lots of Glass Flake



Comparison of Size Degradation of Different Lots of Glass Flake

mix is smaller than 0.0117 inches in length and less than 20% is between 0.0117-0.0232 inches in length. Physical testing of laminates made from glass flake reduced to these sizes and bound with conventional commercial resin systems are poor candidates as high strength structural materials.

#### IV.3.5.3.3. Conclusions

The data indicates that major glass flake degradation occurs during the first 10 minutes of mixing. Normally, Abbe mixing requires 17-30 minutes to produce a uniformly wet out mass. Commercial glass flake varies in flake size distribution from box to box, and from lot to lot. Larger flakes degrade at a rapid rate during premix preparation. The breakdown rate for each sample of glass flake varies. Major glass flake degradation takes place within the first 10 minutes of mixing. Mixing times of less than 10 minutes are required if the +30 mesh or larger flakes are to be present in a premix. As an alternate to short wet mixing times, a mixing process needs to be developed which will provide the degree of wet out without flake size degradation.

#### IV.3.5.4. Glass Breakdown Study - Dry Blends

The objective of this study was to determine whether dry blended laminates, prepared with a controlled flake size, would exhibit mechanical properties which could be correlated to different sizes of mesh. The dry blending method was chosen to mix glass with resin, as this method allowed for formulation of laminate premixes without excess flake breakdown during mixing. Previous experience has demonstrated that the Abbe blender causes degradation of the glass during the mixing cycle. The large flake sizes in particular are subject to deterioration.

To reduce the number of laminates tested, it was postulated that the effect on strength properties of the glass flake as reinforcement would be independent of the resin used in the composite. Therefore, this study was limited to the EL-26 series as a solid pulverized epoxy resin binder system. All the laminates used in this study were composed of 70% glass flake, 2 microns thick. Although a 70% glass content level was chosen, lower glass contents should show similar relationships between flake size and laminate strengths. The resin binder system consisted of Jones Dabney Epi Rez 522 (epoxy), a solid at room temperature. For use, this resin was pulverized and screened into the -100 mesh fraction. Both the pulverized resin and the pulverized hardener were dry blended to produce a homogeneous material in preparation for the blending with glass flake. Classification of glass flake into the chosen particle size range was accomplished using a Sweco Vibro-Screen separator. Five flake sizes were chosen for this study: +8 mesh, +16 mesh, +50 mesh, and the +100 mesh flake sizes.

Glass flake was added to a Patterson-Kelley V blender and tumbled for a period of 1/2 to one hour prior to addition of the resin. After the 1/2 hour blending time, the glass flake had developed a static charge. The pulverized resin and hardener system was then added. A two-hour dry blending time was used. Previous experience indicated that shorter blending time did not give a good coating of the pulverized resin on glass flakes.

Table 44 gives the curing parameters used for the preparation of all the laminates in the series. All were prepared in a 9 x 9 box mold in the 10 x 10 Elmes compression press.

TABLE 44

Summary of Preforming and Curing Parameters for Laminate Preparation  
(Flake Size Study - Laminates EL-26-3 to -10)

P <sub>T</sub>	P <sub>θ</sub>	P <sub>p</sub>	C <sub>T</sub>	C <sub>θ</sub>	C <sub>P</sub>	M <sub>T</sub>	M <sub>θ</sub>	M <sub>P</sub>
170	20-30	200	300	1.5	0	300	2	750

Key:

- P<sub>T</sub> = Preforming temperature, °F.
- P<sub>θ</sub> = Preforming time, seconds
- P<sub>p</sub> = Preforming pressure, psi
- C<sub>T</sub> = Contact temperature, °F.
- C<sub>θ</sub> = Time in which preformed dry blend is allowed to come to molding temperature at contact pressure, subsequently referred to as contact time, minutes.
- C<sub>P</sub> = Contact pressure, psi
- M<sub>T</sub> = Molding temperature, °F.
- M<sub>θ</sub> = Molding time, hours
- M<sub>P</sub> = Molding pressure on laminate, psi

Study shows that when a larger flake size is formulated into a laminate by the dry blend process, it degrades during the molding process into smaller flakes. The effect on strength properties is nearly similar to the effect of smaller flake size in a laminate made by the dry blend premix process.

In Table 45, the glass flake size found after molding is listed together with the original flake size formulated into the premix. It is apparent from the data that the larger flake size as formulated, degraded more during the molding operation than the mixes formulated with smaller flake fractions. The flake size distribution after molding is illustrated graphically in Figure 16.

When the premix containing all +8 mesh glass flake was molded, all of the +8 mesh glass flakes were degraded to a smaller size. The glass flake size analysis, after molding, revealed that only 31.3% of what had been +8 mesh glass flake was retained on the +16 mesh screen. As a contrast, the premix containing all +100 mesh glass flake degraded much less as a result of the molding operation.

Table 45

**GLASS FLAKE DEGRADATION DURING MOLDING  
AS A FUNCTION OF PREMIX GLASS SIZE**

Laminate Identi- fication	Flake Size before molding 100% on	FLAKE SIZE FOUND AFTER MOLDING (per cent)						
		8 mesh	16 mesh	30 mesh	50 mesh	100 mesh	minus 100 mesh	
EL-26-3	8 mesh	0	31.3	20.8	40.3	7.20	0.520	
EL-26-5	16 mesh	0	5.33	25.7	46.2	12.3	10.4	
EL-26-7	30 mesh	0	0	0.62	35.7	42.0	21.6	
EL-26-9	+50 mesh	0	0	0	28.93	52.9	19.8	
EL-26-10	+100 mesh	0	0	0	0	63.1	36.9	



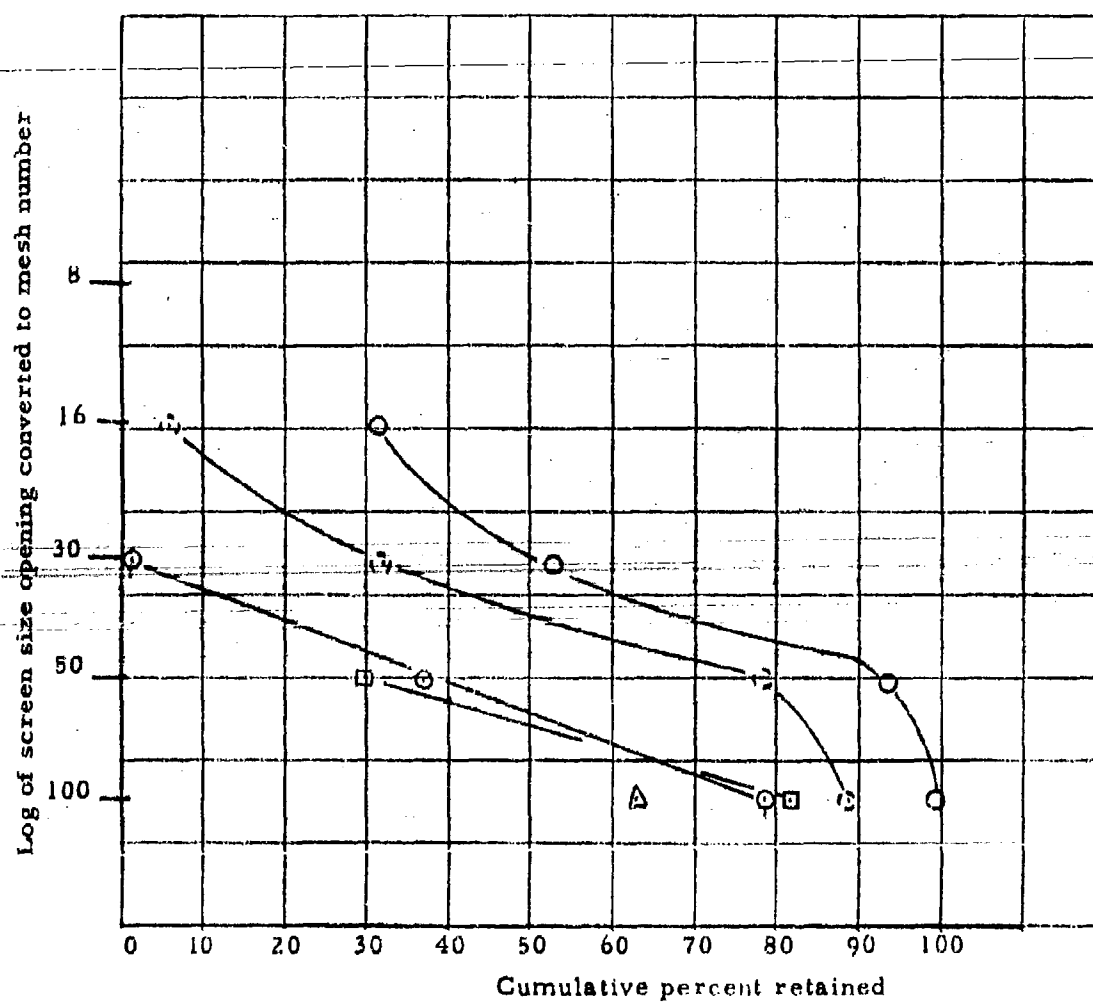


FIGURE 16

Glass Flake Size Distribution  
After Molding of Dry Blended  
Laminates at Conditions Listed  
in Table 3

KEY: Laminates  
100%: prepared with  
○ + 8 mesh  
○ + 16 mesh  
○ + 30 mesh  
□ + 50 mesh  
△ + 100 mesh

After molding of this premix, the glass size analysis revealed that 63.1% of the formulated flake size, +100 mesh, was still retained on the 100 mesh screen. That is, only 36.9% of the formulated glass size was degraded to a smaller size.

Mechanical properties of the laminates prepared in this study are presented in Table 46. From this data, it can be seen that the effect of original flake size on tensile, flexural and compressive strength, is minor. The average tensile properties of the laminates prepared using the +8 mesh flake and +16 mesh flake are slightly higher than the average tensile properties of the laminates formulated with the other three mesh sizes. The standard deviation of the tensile values for the +8 and +16 mesh laminates are 1500-2700 psi. The tensile strengths are therefore within the same range for both laminates. Even though the original glass flake size was +8 mesh as a dry blended premix, during molding it was broken down to a flake size comparable to that of the +16 mesh fraction resulting in the final molded glass flake size distribution similar to that of the +16 mesh premix. (Refer to Figure 16 for distribution of glass flake in the cured laminates.) The three remaining fractions, the +30, the +50 and +100 mesh fractions had slightly lower average tensile strengths than the large flake laminates. The average for these three samples is between one and four thousand lbs. per sq. inch below that of the laminates composed of the coarser glass flake sizes. However, considering the standard deviations for the laminates, 1-3,000 psi, the laminates can be considered of equivalent strength.

Data in Table 46 indicate that tensile modulus values followed a similar pattern as the tensile strength values. The +8 mesh fraction yielded a laminate having the highest tensile modulus of elasticity. This property in laminates of the remaining fractions is lower with the exception of the +50 mesh glass size fraction. There is a general degradation of this tensile modulus as the glass flake size decreases. Although tensile strength does not vary greatly with flake size, it is apparent that the modulus is affected adversely by decreasing flake size.

Flake sizes of +8, +16 and the +30 mesh yielded laminates which have flexural strengths ranging from 32-24,000 lbs. per sq. inch. The flexural properties of the +30 mesh glass size fraction are in the range of 25,900 and 26,800 psi. The degradation of flexural strength values with the very fine glass sizes is similar to the degradation of properties noted for the other stress-strain properties.

The laminates prepared with the +8 mesh glass flake yielded the highest flexural modulus of the entire series. This was a value of 5.33 million psi. The +16 and the +35 mesh laminates had flexural moduli of 4.65 and 4.60 million psi, respectively. Flexural modulus values for the EL 26-9 laminate were not calculated because graphs of the load vs. elongation for these samples were too irregular to give meaningful data. The EL 26-10 laminate composed of the +100 mesh glass flake had the lowest flexural modulus of the series, 3.92 million psi. As was the case in tensile properties, the +8 mesh and the +16 mesh and the +35 mesh glass fractions have given similar flexural properties while the very fine flake, the +100 mesh, gave the lowest average ultimate strength values.

TABLE 46

## SULFATION OF GLASS FLAKE SIZE STUDIES AND MECHANICAL PROPERTIES

Laminates Identified AS-100	% Glass	Density	Glass flake size (initial)	Tensile Strength $\times 10^5$ psi		Tensile Modulus $\times 10^6$ psi		Flexural Strength $\times 10^3$ psi		Flexural Modulus $\times 10^6$ psi		Compressive Strength $\times 10^4$ psi		Compressive Modulus $\times 10^6$ psi	
				Average	$\sigma$	Average	$\sigma$	Average	$\sigma$	Average	$\sigma$	Average	$\sigma$	Average	$\sigma$
EL 26-1*	70	1.93	Unc1.	12.24	2.44 n=5	-	-	4.78	n=6	4.58	n=6	1.436	16.02 n=5	1.018	.814 n=5
EL 26-2*	70	1.99	Unc1.	15.01	1.13 n=6	-	-	3.38	n=5	4.62	n=5	1.927	-	1.280	-
EL 26-3	70	1.859	-8	12.86	2.72 n=6	4.435	-	2.72	n=6	5.28	n=6	1.86	-	.880	-
EL 26-5	70	1.884	-3+16	12.408	1.57 n=6	3.708	2.45 n=5	4.62	n=5	4.65	n=5	1.636	4.61 n=5	1.132	.634 n=5
EL 26-7	70	1.889	-16+30	9.336	3.25 n=5	3.093	-	5.91	n=5 Not Valid	4.605	n=5	1.88	-	1.060	-
EL 26-9	70	-	-30+50	11.701	1.52 n=6	3.96	-	2.82	n=5	4.39	n=5	1.457	-	.985	-
EL 26-10	70	1.900	-50+100	11.066	1.42 n=6	3.38	-	5.02	n=6	3.92	n=6	1.675	-	.933	-

KEY:  $\sigma$  = Standard Deviation

n = Number of samples tested

\*EL-26-1 &amp; 2 - Performed with freshly pulverized resin. All others prepared with aged resin.

Tensile Strength

Flexural

Compression

Performed in accordance with  
ASTM D638-58T  
ASTM D790-58T  
ASTM D695-56

## 95% Confidence Limits

	95% CL Tensile Str. $\times 10^3$	95% CL Tensile Mod. $\times 10^6$	95% CL Flex. Str. $\times 10^3$	95% CL Flex. Mod. $\times 10^6$
EL 26-1	11.26 $\leftrightarrow$ 15.22	-	34.43 $\leftrightarrow$ 24.39	5.26 $\leftrightarrow$ 3.90
EL 26-2	17.22 $\leftrightarrow$ 16.80	-	35.21 $\leftrightarrow$ 26.83	4.79 $\leftrightarrow$ 4.45
EL 26-3	5.72 $\leftrightarrow$ 16.00	-	36.26 $\leftrightarrow$ 30.54	6.57 $\leftrightarrow$ 5.99
EL 26-5	14.06 $\leftrightarrow$ 10.76	6.75 $\leftrightarrow$ 0.67	37.86 $\leftrightarrow$ 26.40	5.37 $\leftrightarrow$ 3.93
EL 26-7	2.75 $\leftrightarrow$ 5.93	-	-	-
EL 26-9	12.80 $\leftrightarrow$ 9.60	-	30.35 $\leftrightarrow$ 23.35	5.05 $\leftrightarrow$ 3.73
EL 26-10	14.66 $\leftrightarrow$ 7.48	-	31.24 $\leftrightarrow$ 20.50	4.61 $\leftrightarrow$ 3.23

The compressive strength values of the entire series showed no general definite correlation with glass flake size. Compression strength of resin forced plastic composites is usually a measure or a function of the resin system used. Therefore, it was expected that no relation of flake size to compressive strength would occur.

An alternate solid resin system was developed which was used for a glass flake size and mechanical property study. The average tensile values of the laminates prepared with 70% glass (unclassified flake) were 16,000 and 18,000 lbs. per sq. inch, as shown in Table 46. The tensile values of the test series in question are much lower than should be expected, because both the pulverized resin and the pulverized hardener used in the formulations were stored at room temperature for one to two weeks. Both the epoxy resins and the hardener were hygroscopic and absorbed water at room temperature. This led to general deterioration of strength properties. Laminates EL-26-1 and -2 were prepared with fresh resin and hardener systems. These laminates, in contrast, gave much higher average strength properties as shown in Table 46. These results indicate the advantage of pulverizing and storing both the epoxy resin system and the hardener in a low humidity atmosphere prior to mixing.

#### IV.3.5.4.1. Conclusions

This study has illustrated that the original glass flake size formulation into dry blended laminates does not markedly affect glass flake composite strengths. However, flexural and tensile modulus appears to be decreased with decreasing flake size. The +8 mesh, +16 mesh and +30 mesh glass flake sizes have given slightly higher tensile and flexural strengths than the finer sizes. The +8 to +30 mesh glass flake size comprises approximately 80% of the distribution of the random glass flake as received, and the mechanical properties for laminates made with these fractions are similar; therefore, molding of dry blended composites should be restricted to using only these or larger glass flake sizes.

#### IV.3.5.5. The Effect of Processing Procedure on Final Glass Content and Laminate Strength Properties

Using EL-23 epoxy based on 50% glass resin systems, (Table 47) five laminate sheets were molded at four pressure levels. The object of the study was to compare properties of Abbe premixes that had been preoriented and degassed of air inclusions to a premix that had not been so treated. A secondary objective was to determine whether high glass content laminates could be obtained by using molding pressure to squeeze out excess resin.

The method consisted of calendering on the hand operated 2-roll calender, degassing the precut, measured sheet in a vacuum oven for one hour at 0.1 mm. Hg, placing the degassed sheet into the preheated compression mold and curing the sheet at the required pressure and temperature and cycle of time (Table 48).

T A B L E 47

DISTRIBUTION OF GLASS FLAKE IN  
CURED LAMINATE EL-23-2

Mesh Size	Premix Before Molding-After Mixing		Center Composite		Top & Bottom - Edge & Composite	
	Individual	Cumulative	Individual	Cumulative	Individual	Cumulative
8	0.7	0.7	0	0	0	0
16	3.0	3.7	0	0	0	0
30	27.8	31.5	2.3	2.3	0.2	0.2
50	30.3	61.8	44.0	46.3	29.8	30.0
100	20.1	81.9	27.3	73.6	33.6	63.6
Pan	16.5	98.4	24.2	97.8	35.7	99.3
Glass Content	60%		77.5%		79.7%	

## Resin Formulation:

Jones Dabney Epi-Rez 509 69.4 g. Epoxy Resin  
Methyl Nadic Anhydride 62.5 g. Curing Agent  
DMP-10 1.4 g. Accelerator

## Glass Content:

60% At Start  
+8 Mesh 2 Micron Glass Flake  
Final Glass Content: Determined at  $\pm 1\%$

## Abbe Mix:

5 Mins. at 130° F.

Cure: Compression Molded. (0.100 in. thick)  
2 hrs. 200° F. 1000 psi  
2 hrs. 400° F. Oven

**TABLE 48**  
**RELATIONSHIP OF FINAL GLASS CONTENT TO MOLDING PRESSURE**  
**FOR COMPRESSION MOLDED EPOXY-GLASS FLAKE SHEETS (SERIES EL-23)**

Identification	Premix Preparation	Curing Cycle Time & Temp. "C" Hydraulic System Press.	Final Glass Content % Weight	Cured Sheet Appearance
EL-23-4	A	250	69-70	Clear - Void Free
EL-23-5		250	Sample Retained For Display	Clear - Void Free
EL-23-6		500	73	Clear - Void Free
EL-23-7		750 Wide Press. Fluctuations	72	Delamination Apparent Within Various Sections of the Sheet
EL-23-8	B	500 Wide Press. Fluctuations	74	Visible Air Pockets Also Delaminated Sections Visible

"C" Conditions in procedure.

SUPPLEMENT TO TABLE 48Premix Preparation (EL-23-Series)

**A - Formulated as 50% + 8 mesh glass flake & 50% Resin**

**Resin Composition:** Jones Dabney (Epoxy) 509 - 100 parts  
 Methyl Nadic Anhydride 90 parts  
 DMP-10 2 parts

**Mixed in Abbe Mixer 5 minutes**

**Mixer Jacket Temperature 130-150° F.**

**Premix: Calendered to 0.100 sheet**

**Degassed for 1 hr. at 0.5 mm. Hg**

**Molded in 12 x 12 "Watson Stillman Press**

**Molding: Step 1 - 2 hrs. 200° F. at indicated pressure**

**(C) Step 2 - 2 hrs. 350° F. in oven**

**B - Formulated as 60% + 8 Mesh glass flake & 40% resin**

**Resin Composition: Same as A**

**Mixing: Same conditions as B**

**Premix: Stacked without orientation & degassing into preheated  
 10 x 10 mold**

**Molding: Step 1 - same as A**

**(C) Step 2 - same as A**

**\*Molding Pressure - for Sheets No. 7 and 8 fluctuated during cure-  
 Responsible for delamination within sheet.**

The relationship between molding pressure during cure and final glass content is shown graphically in Figure 17. The position and location from which samples were cut to determine glass flake distribution within a glass flake laminate are shown in Sketch 6.

The tensile and flexural properties of the laminates are presented in Table 49. Examination of the data reveals the benefits in increased physical properties obtained through degassing and orientation.

Figures 18 and 19 compare the glass flake size distribution after blending and after molding. The data shows that glass flake fines will flow to a greater extent than larger flakes; therefore, a higher percentage of large flakes are retained in the center of the laminate.

Data in Tables 50, 51, and 52 were obtained from a similar study using the multiple-calender roller assembly to process the sheet. The data indicates that laminates produced from calender oriented sheets contain the same glass flake size distribution as the process premix. Therefore, apparently if the preform sheet is highly oriented, high compression molding pressures do not have the degrading effect experienced in molding bulk premixes.

#### IV.3.5.5.1. Conclusions

The process of orienting and degassing premixes yields laminates with increased tensile and flexural strengths and lower void content. Molding pressure can be raised to control final glass content, however, final glass content attainable is a function of mold clearance. At 0.008" clearance, a 78% glass content was obtained from a 50% glass premix. The control over final premix composition is nonexistent; prediction of the value was pure guesswork on the part of the operator. Therefore, although the glass content can be increased, this is not a suitable production method.

Flow of fine glass flake takes place from the center of the laminate to the outer edges leaving larger flakes in the center. Extensive crushing of non-oriented glass flake particles occurs during the molding cycle when pressures of 1000 psi are used. The degradation of flake is reduced by orientation of the flake.

It was data from this study which revealed the potential value of the proposed roller-orientation process and gave incentive to more detailed study of that phase of the program.

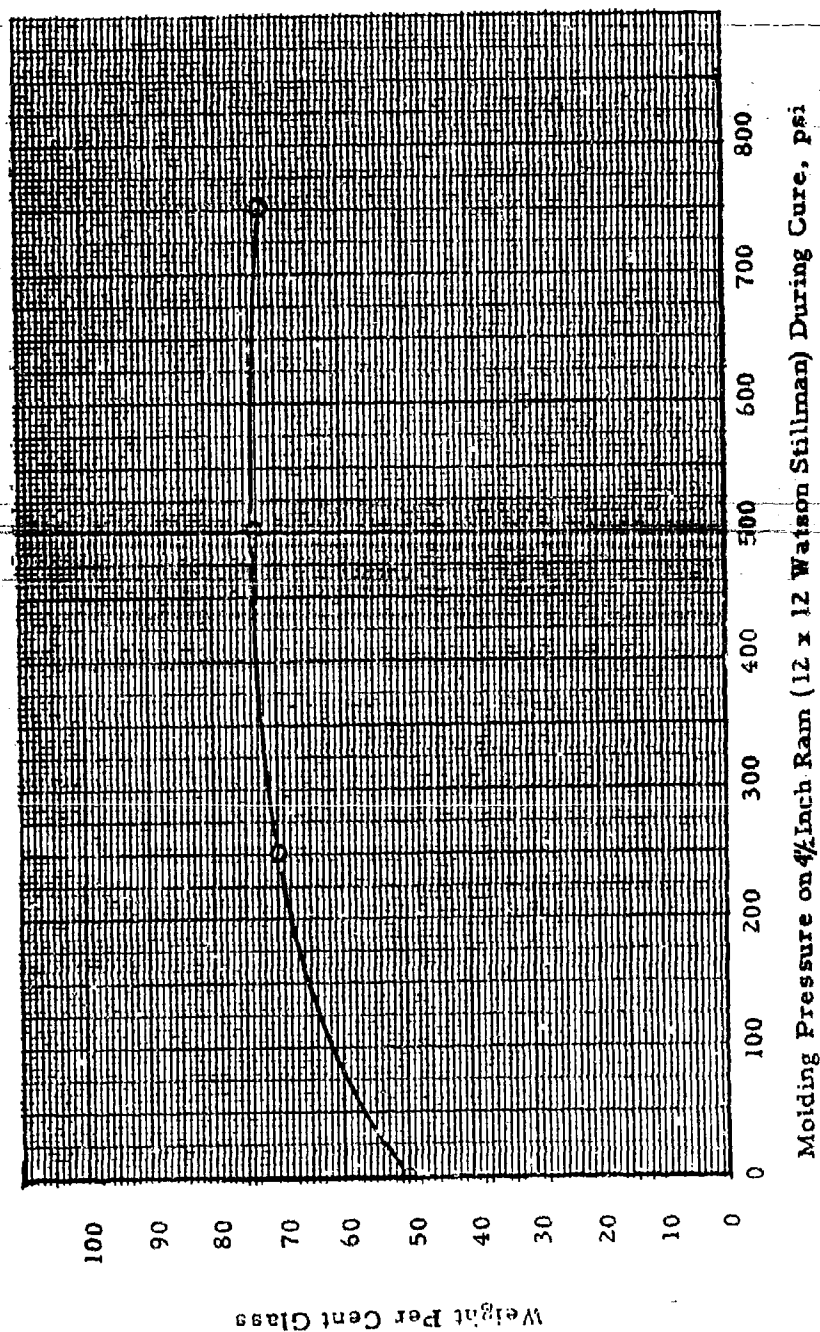
#### IV.3.5.5.2. Effect of Roller Calendering Upon Physical Properties

The study was designed to reduce the large number of process and raw material variables encountered (except variations in wet flake treatment), in the preparation of laminates from oriented (calendered) and non-oriented premixes. The effect of glass flake content upon laminate strength and visual quality was also evaluated.



Figure 17

THE EFFECT OF CURE PRESSURE ON FINAL GLASS CONTENT  
OF COMPRESSION MOLDED GLASS FLAKE-EPCXY SHEETS



75.7 %	79.7 %	75.7 %				
<table><tr><td>74.6</td><td>78.3</td><td>79.0</td><td>77.5</td></tr></table> <p>(77.5 % Av.)</p>			74.6	78.3	79.0	77.5
74.6	78.3	79.0	77.5			
79.7 %						

Sketch 6

G LASS CONTENT DISTRIBUTION  
 WITHIN CURED LAMINATE SHEET (9 x 9 inch)

EL-23-2

TABLE 49

**TENSILE & FLEXURAL STRENGTH, LAMINATE PROPERTIES  
FOR EL-23-4 TO EL-23-8 COMPRESSION MOLDED SHEETS**

Identification	Thickness In.	Density G./cc	% Voids	Average Tensile Strength psi $\times 10^{-3}$	Std. $\sigma$ Deviation psi $\times 10^{-3}$	Average Tensile Modulus psi $\times 10^{-6}$	Std. $\sigma$ Deviation psi $\times 10^{-6}$	Average Flexural Strength psi $\times 10^{-3}$	Flexural Modulus psi $\times 10^{-6}$
EL-23-4	0.076	1.943	0	19.1	1.3 n=4	7.12	- n=2	23.8	3.30
EL-23-6	0.086	1.991	0	16.1	2.7 n=3	6.22	1.20 n=3	28.4	4.01
EL-23-7	0.063	1.946	6.0	9.4	1.6 n=3	6.79	1.60 n=4	26.4	3.89
EL-23-8	0.118	1.935	2.0	6.2	1.2 n=3	5.32	- n=2	10.2	2.94

\*n = no. samples

EL-23-8 No orientation or degassing

**95% Confidence Limits**

	95% CL Tensile Str. $\times 10^3$	95% CL Tensile Mod. $\times 10^6$
EL 23-4	21.2 $\leftrightarrow$ 17.0	-
EL 23-6	18.4 $\leftrightarrow$ 13.8	7.22 $\leftrightarrow$ 5.22
EL 23-7	10.7 $\leftrightarrow$ 8.1	9.34 $\leftrightarrow$ 4.24
EL 23-8	7.2 $\leftrightarrow$ 5.2	-

FIGURE 18

Bar Graph of Individual Screen Analysis for Premix and  
Cured Compression Molded Epoxy - Glass Flake Sheet (EL-23-2)

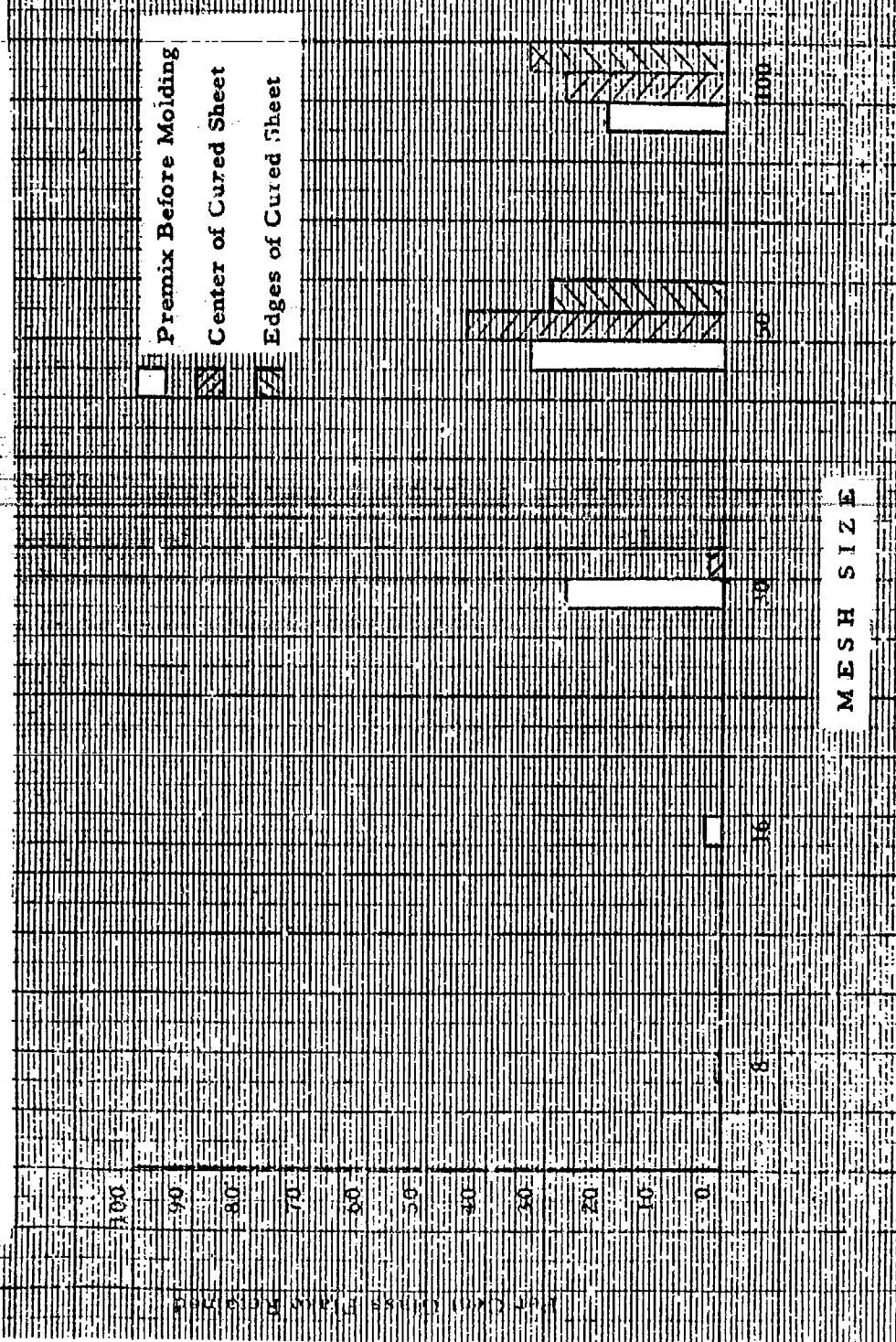


FIGURE 19

Distribution Plot of Individual Screen Analyses for Premix and  
Cured Compression Molded Epoxy-Glass Flake Sheet (EL-23-2)

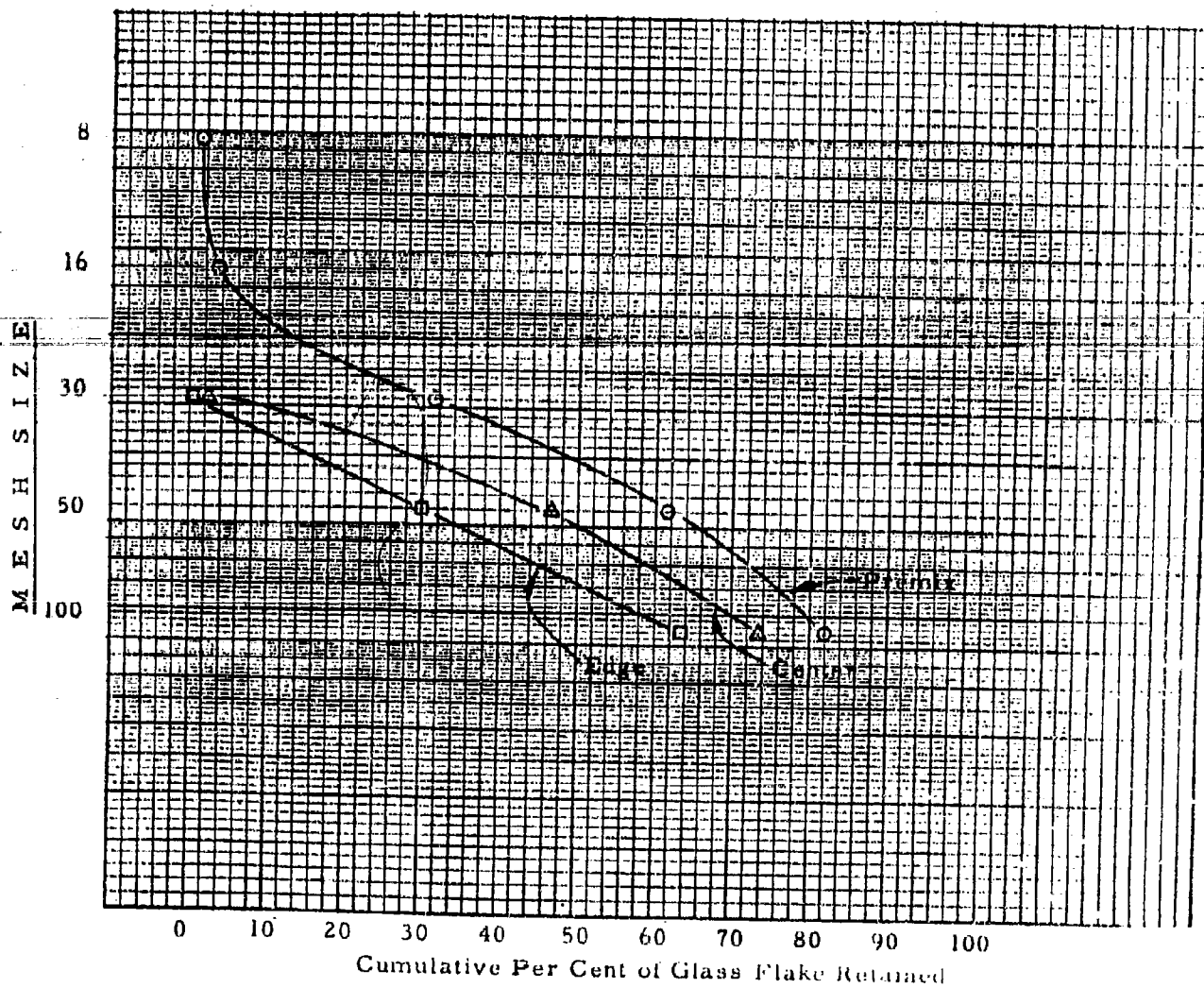


TABLE 50Glass Flake Breakdown Study 60/40

	<u>% +4</u>	<u>% +8</u>	<u>% +16</u>	<u>% +30</u>	<u>% +50</u>	<u>% +100</u>	<u>% Pan</u>	<u>% Loss</u>	<u>% Glass</u>
Original Glass*	70.7	14.6	8.5	1.8	1.3	0.5	0.4	2.1	
Original Glass**	54.2	20.4	11.0	3.4	4.6	3.4	1.7	1.3	
Wet Premix - *	-	-	-	0.6	18.1	38.3	42.5	0.5	59.8
Orientated 1st Pass	-	-	-	0.8	22.7	39.3	36.7	0.5	60.0
Molded Sheet ELR 3-5	-	-	-	0.4	12.4	38.1	47.6	1.5	60.4

\*Original Glass came from two different boxes

\*\*No vacuum used in mixing

TABLE 51

Glass Flake Breakdown Study

	<u>% +8</u>	<u>% +16</u>	<u>% +30</u>	<u>% +50</u>	<u>% +100</u>	<u>% Pan</u>	<u>% Loss</u>
Original Glass	73.6	11.5	5.1	6.0	2.9	2.0	2.0
Wet Premix	-	0.1	0.5	14.5	35.4	47.6	1.9
Wet Premix from Abbe Side Walls	-	Trace	0.5	9.7	33.9	54.2	1.7
Premix from Ram Extruder	-	Trace	0.5	12.4	36.7	48.0	2.4
Orientated 1st Pass	-	Trace	0.4	10.2	34.4	52.3	2.7
Orientated 2nd Pass	-	0.1	0.3	8.5	31.9	57.1	2.1
Hand-Feed 1st Pass	-	Trace	0.6	12.0	39.7	47.5	0.2
Molded Sheet	-	-	0.4	10.6	32.0	54.9	2.2

Wet Premix - 60/40 Glass/Epoxy

Original Glass - Classified Flake (+8 Mesh)

TABLE 52

## Glass Flake Breakdown Study

	<u>% +8</u>	<u>% +16</u>	<u>% +30</u>	<u>% +50</u>	<u>% +100</u>	<u>% Pan</u>	<u>% Loss</u>
Original Glass	73.6	11.5	5.1	6.0	2.9	2.0	2.0
Wet Premix	-	Trace	2.1	29.1	35.3	32.2	1.3
Orientated 1st Pass	-	0.7	4.6	25.6	37.5	31.5	0.1
Orientated 2nd Pass	-	0.1	5.2	30.7	40.2	23.0	0.8
Molded Sheer 1st Pass Material	-	-	1.5	23.4	37.4	37.6	0.1

Wet Premix 50/50

Original Glass - Classified Flake (+8 Mesh)



The premixes were prepared in the Abbe mixer using a tightly time controlled blending procedure. The glass flakes were added to the preblended resin over a 10 minute period of time. The blending was continued for exactly 20 minutes after the last flake was added. Lowest blade speed was used during the addition period and highest speeds during the mixing period. The blended material divided into two portions for processing which were treated as described below.

One portion of the premix was processed through the roller-calender assembly into oriented sheets, stored at ambient temperatures 25 hours until B-staged, cut into the correct size and weight of preform, charged into the preheated mold cavity for a specified length of time, and cured under rigid molding conditions (Table 53). These laminates are designated ELR4 series. Two laminates 1/16" and 1/8" thick were molded for each glass flake content 50%, 60% and 70%.

The second portion of the wet, unoriented premix was preweighed, charged directly into the preheated mold, preheated for a specific length of time and molded under rigid molding conditions (Table 53). These laminates are designated ELU4 series.

The physical properties of the laminates are listed in Tables 54 and 55, together with calculated confidence limits of the data at 95% level. It can be seen that generally superior properties were obtained from the calendered flake. Significant improvement in tensile properties were realized, although the improvement of other properties were not as spectacular.

It should be noted that the calender oriented sheets used in this study exhibited a major defect which results from warpage of the wooden rolls in the assembly. The effect of this warpage produces variations of sheet thickness along the calendered length. This thick portion represents an area of lessened compression pressure on the premix. The wavy sheet effect is shown in Photograph 32. Use of an improved roller calender assembly would result in elimination of this defect with resulting significant increases in properties.

The tensile strength of the ELR4 series was apparently unaffected by glass content, the tensile modulus of the 70% glass series was the highest recorded for the study.

The glass flake size distribution of the specimens after mixing, after processing and after molding was determined using the techniques described in this report. The results of this phase of the study are of major importance. It was determined that the chemical composition of the glass flakes used in this study differed from the previous glass flake supplied. This glass flake dissolved (up to 50%) in nitric acid. All data reported for the later series of experiments may be suspect since the chemical composition of the glass may effect resin bond, glass flake properties and glass flake laminate properties.

Table 53  
Effect of Processing Upon Physical Properties  
Process and Molding Parameters of Laminates

<u>Sample</u> <u>Ident.</u>	<u>Cal</u>	<u>"B"</u> <u>Staged</u>	<u>Pre-</u> <u>Heat</u>	<u>Contact</u> <u>Pres.</u>	<u>Contact</u> <u>Temp.</u>	<u>Contact</u> <u>Time</u>	<u>Molding</u> <u>Pres.</u>	<u>Molding</u> <u>Temp.</u>	<u>Molding</u> <u>Time</u>
ELU 4-1	No	No	-	0	300°F	6 mins.	2500 lb.	300°F	60 mins.
ELR 4-1	Yes	Yes	-	0	300°F	3 mins.	2500 lb.	300°F	30 mins.
ELU 4-2	No	No	-	0	300°F	6 mins.	2500 lb.	300°F	60 mins.
ELR 4-2	Yes	Yes	-	0	300°F	3 mins.	2500 lb.	300°F	30 mins.
ELU 4-3	No	No	-	0	300°F	6 mins.	2500 lb.	300°F	60 mins.
ELR 4-3	Yes	Yes	-	0	300°F	3 mins.	2500 lb.	300°F	30 mins.
ELU 4-4	No	No	-	0	300°F	6 mins.	2500 lb.	300°F	60 mins.
ELR 4-4	Yes	Yes	-	0	300°F	3 mins.	2500 lb.	300°F	30 mins.
ELU 4-5	Yes	Yes	-	0	300°F	3 mins.	2500 lb.	300°F	30 mins.
ELR 4-5	Yes	Yes	-	0	300°F	3 mins.	2500 lb.	300°F	30 mins.
ELU 4-6	No	No	-	0	300°F	6 mins.	2500 lb.	300°F	60 mins.
ELR 4-6	Yes	Yes	-	0	300°F	3 mins.	2500 lb.	300°F	30 mins.

TABLE 54  
EFFECT OF PROCESSING UPON PHYSICAL PROPERTIES  
ORIENTED AND NON-ORIENTED

Sample Ident.	% Glass Flake	Glass Flake Size	Tensile Str. $\times 10^3$ psi av.	EL Mod. $\times 10^6$ av.	Comp. Str. $\times 10^4$ psi av.	Std. Dev. $6 \times 10^4$ psi	Comp. Mod. $\times 10^6$ psi av.	Std. Dev. $6 \times 10^6$ psi	Flex. Str. $\times 10^3$ psi av.	Std. Dev. $6 \times 10^3$ psi	Flex. Mod. $\times 10^6$ psi av.	Std. Dev. $6 \times 10^6$ psi	Laminate Thickness Inches
ELU4-1	50	Uncl.	6.74	1.82	1.49	n=6 .39	1.85	n=6 .29	6.4	n=4 1.54	1.22	n=4 .15	1/8
ELR4-1	50	Uncl.	8.66	1.88	2.72	n=5 .63	1.99	n=5 .34	9.6	n=3 1.58	1.65	n=3 .04	1/8
ELU4-2	50	Uncl.	5.46	1.55	2.54	n=6 .38	1.50	n=6 .27	9.2	n=5 1.75	1.72	n=5 .29	1/4
ELR4-2	50	Uncl.	9.21	2.03	2.93	n=6 .27	1.75	n=6 .06	10.8	n=4 1.54	1.63	n=4 .02	1/4
ELU4-3	60	Uncl.	2.85	-	1.28	n=6 .40	1.95	n=6 .26	6.8	n=4 .46	1.50	n=4 .23	1/8
ELR4-3	60	Uncl.	9.81	2.36	2.63	n=6 .49	2.28	n=6 .20	7.7	n=5 1.33	1.81	n=5 .16	1/8
ELU4-4	60	Uncl.	3.21	1.97	2.14	n=6 .25	1.78	n=6 .42	6.5	n=5 1.01	2.10	n=5 .15	1/4
ELR4-4	60	Uncl.	8.39	1.80	3.03	n=6 .22	2.36	n=6 .22	9.3	n=5 1.72	2.25	n=5 .71	1/4
ELU4-5	70	Uncl.	5.76	3.20	2.20	n=6 .29	2.10	n=6 .65	8.9	n=4 .78	1.97	n=4 .17	1/8
ELR4-6	70	Uncl.	4.66	2.00	2.22	n=8 .14	1.53	n=8 .31	6.0	n=3 2.02	1.62	n=3 .23	1/4
ELR4-6	70	Uncl.	8.20	3.56	2.32	n=6 .56	1.88	n=6 .69	8.9	n=4 .97	2.31	n=4 .10	1/4

Table 55  
Effect of Processing Upon Physical Properties

Confidence Limits for Table 54

	95% CL Comp. Str. $\times 10^4$	95% CL Comp. Mod. $\times 10^6$	95% CL Flex. Str. $\times 10^3$	95% CL Flex. Mod. $\times 10^6$
ELU 4-1	1.90 $\leftrightarrow$ 1.08	2.15 $\leftrightarrow$ 1.55	8.8 $\leftrightarrow$ 4.0	1.46 $\leftrightarrow$ .98
ELR 4-1	3.50 $\leftrightarrow$ 1.94	2.41 $\leftrightarrow$ 1.57	13.5 $\leftrightarrow$ 5.7	1.75 $\leftrightarrow$ 1.55
ELU 4-2	3.04 $\leftrightarrow$ 2.24	1.79 $\leftrightarrow$ 1.21	11.4 $\leftrightarrow$ 7.0	2.09 $\leftrightarrow$ 1.35
ELR 4-2	3.22 $\leftrightarrow$ 2.64	1.81 $\leftrightarrow$ 1.69	13.2 $\leftrightarrow$ 8.4	1.66 $\leftrightarrow$ 1.60
ELU 4-3	1.70 $\leftrightarrow$ 0.86	2.22 $\leftrightarrow$ 1.68	7.5 $\leftrightarrow$ 6.1	1.87 $\leftrightarrow$ 1.13
ELR 4-3	3.15 $\leftrightarrow$ 2.12	2.49 $\leftrightarrow$ 2.07	11.3 $\leftrightarrow$ 8.1	2.01 $\leftrightarrow$ 1.61
ELU 4-4	2.40 $\leftrightarrow$ 1.88	2.22 $\leftrightarrow$ 1.34	7.8 $\leftrightarrow$ 5.2	2.29 $\leftrightarrow$ 1.91
ELR 4-4	3.26 $\leftrightarrow$ 2.80	2.49 $\leftrightarrow$ 2.03	11.4 $\leftrightarrow$ 7.2	3.13 $\leftrightarrow$ 1.37
ELR 4-5	2.50 $\leftrightarrow$ 1.90	2.78 $\leftrightarrow$ 1.42	10.1 $\leftrightarrow$ 7.7	2.24 $\leftrightarrow$ 1.72
ELU 4-6	2.34 $\leftrightarrow$ 2.10	1.79 $\leftrightarrow$ 1.27	11.0 $\leftrightarrow$ 1.0	2.19 $\leftrightarrow$ 1.05
ELR 4-6	2.91 $\leftrightarrow$ 1.53	2.60 $\leftrightarrow$ 1.16	10.4 $\leftrightarrow$ 7.4	2.47 $\leftrightarrow$ 2.15

Glass flake laminates were digested in nitric acid to remove the resin binder without effecting the glass flake content in all studied described in this report. The premix, oriented sheet and laminates were submitted to the same digestion process to determine the effect of processing and molding upon glass flake particle size distribution. The results obtained are listed in Table 56 and show that excessive loss of glass flake contents were encountered.

Exhaustive investigation showed that the weighed quantities of ingredients used in preparation of the premix were correct, that the balances used to weigh the ingredients and specimens were in proper working order. Therefore, the tests shown in Table 57 were performed. The results reveal that the glass flake in the new batches (Boxes A to G) was different from the older sample of flake representing material used in early development.

As part of the early phases of the program an anhydride cured-epoxy laminate was produced which exhibited the highest tensile value (21,800 psi) recorded during the entire program. Because of the emphasis on process know-how, development and production of prototype parts, this interesting lead was not investigated further at the time. After consideration of the improvements of strength noted in use of calender oriented material, an attempt was made to duplicate the earlier experiment to see if newly developed techniques would cause increases of tensile strength.

The blend (Tables 58 and 59) was Abbe premixed and calender oriented into flat sheets. The sheet was cut into 9 X 9 inch squares, removed from the heavy parting paper and placed between mylar sheet prior to exposure to the vacuum and subsequent molding. Trimming one inch from all the edges removed all traces of occluded air from the laminate.

The molded units which were produced were of visually superior quality, highly transparent and free from all visual defects such as air bubbles, check or flow lines and misoriented opalescent areas.

Physical test data for these laminates are presented in Table 58. The tensile strength did not reach the high 21,800 psi value previously reported for the system.

The low tensile values exhibited by these apparently perfect laminates are discouraging. Only three factors could be causing these low values. 1) Glass flake degradation may have been excessive; because the glass is acid soluble this could not be determined. 2) The glass flake laminates have a tensile strength limit which is in the reported range, and 3) the change in glass flake chemical composition has adversely effected the physical properties.

Tables 60 and 61 list the physical properties, 95% confidence limits and molding parameters of a variety of laminates produced in efforts to determine a number of concepts investigated in support of the developments described in this report.

Photograph 32



Roller Calendered Oriented Premix Sheet

Table 56

**Effect of Nitric Acid  
Upon Glass Flake Laminates**

	<u>Resin Wt.</u>	<u>Glass Wt.</u>	<u>% Resin Calc.</u>	<u>% Glass Calc.</u>	<u>% Resin Anal.</u>	<u>% Glass Anal.</u>	<u>% Loss</u>
ELU 4-5 & 6	1284 g	3000 g	30	70	52.3	47.7	32.0
ELR 4-5 & 6	1284 g	3000 g	30	70	52.9	47.1	33.0
ELU 4-3 & 4	2000 g	3000 g	40	60	46	54	10.0
ELR 4-3 & 4	2000 g	3000 g	40	60	58.9	41.1	32.0
ELU 4-1 & 2	2000 g	2000 g	50	50	68.6	31.4	37.0
ELR 4-1 & 2	2000 g	2000 g	50	50	77.9	22.1	55.0
ELR 3-14	2666.6g	4000 g	40	60	40.5	59.5	0.83
ELR 3-5	2666.6g	4000 g	40	60	39.6	60.4	0.67
EL 23-8	133.3g	200 g	40	60	40.1	59.9	0.16
EL 23-2	133.3g	200 g	40	60	40.6	59.4	0.10
EL 23-4	199.9g	200 g	50	50	49.8	50.2	0.40

Table 57

Effect of Nitric Acid on Glass Flakes

	Undried Glass Flake			
	Digest- ion Time	Sple. Wt. Before	Sple. Wt. After	% Loss

Acid Digested  
Glass Flake  
From 1st  
Shipment

3 hrs. 2.0841g 2.0755g 0.41

Acid Digested  
Glass Flake  
From Last  
Shipment

3 hrs. 21.1452g 15.3982g 27.2

Original Glass Flake by Formulation		
Resin	Glass	%Glass

Combustion of  
ELR & ELU 4  
Series 5 & 6

1284g 3000g 70

	Dried Glass Flake			
	Digest- ion Time	Sple. Wt. Before	Sple. Wt. After	% Loss

Drying  
Time Temp.

3 hrs. 1.9240g 1.9227g 0.067 4 hrs. 120°C

21.1452g 15.3570g 27.4 3 hrs. 1100°F

Glass Flake after Combustion 1100°F for 3 Hours			
Sple. Wt. Before	Sple. Wt. After	% Glass	

1.3690g 0.9774g 71.4



TABLE 58

ORIENTED AMBROID CURED EPOXY SYSTEMS  
LAMELLE PROPERTIES

Sample Ident.	% Glass Flake	Glass Flake Size	Tensile Str. $\times 10^3$	Std. Dev. $6 \times 10^3$	EL Mod. $\times 10^6$	Std. Dev. $6 \times 10^3$	Comp. Str. $\times 10^3$	Std. Dev. $6 \times 10^3$	EL Mod. $\times 10^6$	Std. Dev. $6 \times 10^3$	Flex. Str. $\times 10^3$	EL Mod. $\times 10^6$
			Psi av.	Psi	Psi av.	Psi	Psi av.	Psi	Psi av.	Psi	Psi av.	Psi av.
ANEP I	50	5incl.	12.46	$n=5$ 1.34	3.49	$n=5$ 1.08	23.10	-	2.47	-	26.46	3.20
ANEP II	50	5incl.	13.13	$n=5$ 1.67	3.28	$n=5$ 1.81	32.18	$n=6$ 3.7	3.71	$n=6$ .47	23.65	3.34

Calculated Confidence Limits

	95% CL Tensile Str. $\times 10^3$	95% CL Tensile Mod. $\times 10^6$	95% CL Comp. Str. $\times 10^3$	95% CL Comp. Mod. $\times 10^6$
ANEP I	14.12 $\leftrightarrow$ 10.80	4.83 $\leftrightarrow$ 2.15	-	-
ANEP II	15.20 $\leftrightarrow$ 11.06	4.23 $\leftrightarrow$ 2.28	36.07 $\leftrightarrow$ 28.29	36.56 $\leftrightarrow$ 35.58

Formula for Calculation of Confidence Limit

$$CL = \bar{x} \pm t \frac{(M-L)S}{\sqrt{n}}$$

$M$  = No. test specimens

$\bar{x}$  = Mean average

$t$  = Value in table (n-1 degrees of freedom);  
for 95% confidence  $L = 0.05$

$S$  = Standard deviation

Table 59

**Oriented Anhydride Cured Epoxy System**  
**Molding Parameters Used**

Resin System	JD 509	1041 g
	Methyl Nadic Anhydride	937 g
	DMP-10	21 g
Glass Flake	Box D	2000 g
Abbe Blended - roller calender oriented		
Cut into 9 x 9 inch sheets		
Exposed to vacuum		
	1 hour 4-5 mm. Hg	No weights
	1 hour 4-5 mm. Hg	Under 38 lb. weight

Cooled to remove parting film

**Cure Parameters**

Pressure, psi	200
Temperature, °F	250
Time, Hours	2
Cooled to 150°F before opening mold	

TABLE 60

## PHYSICAL PROPERTIES OF UNIMATED SHEET LAMINATES

Sample Identification	% Glass Flake	Glass Flake Size	Tensile Str. $\times 10^3$ PSI	EL Mod. $\times 10^4$ PSI	Comp. Str. $\times 10^4$ PSI	Std. Dev. $\times 10^4$ PSI	Comp. Mod. $\times 10^6$ PSI	Std. Dev. $\times 10^6$ PSI	Flex. Str. $\times 10^3$ PSI	Std. Dev. $\times 10^3$ PSI	Flex. Mod. $\times 10^6$ PSI	Std. Dev. $\times 10^6$ PSI	Laminate Thickness Inches
ELR3-1	60	+8	7.21	2.32	3.15	$n=5$ .33	2.06	$n=6$ .20	10.7	$n=4$ .13	1.94	$n=4$ .11	1/4
ELR3-6	50	Unc1.	6.90	2.59	1.34	$n=5$ .27	2.00	$n=6$ .19	10.0	$n=4$ 1.08	1.75	$n=4$ .10	1/4
ELR3-9	50	Unc1.	5.95	1.62	1.31	$n=5$ .59	2.00	$n=6$ .41	10.3	$n=4$ 1.10	1.74	$n=4$ .05	1/8
ELR3-12	50	Unc1.	12.82	2.65	3.24	$n=5$ .53	2.94	$n=6$ .79	12.9	$n=4$ 1.94	1.46	$n=4$ .36	1/8
ELR3-15A	50	+8	10.71	2.28	2.74	$n=8$ .58	1.86	$n=8$ .50	10.8	$n=5$ 1.57	1.72	$n=5$ .06	1/4
ELR3-15B	60	+8	11.40	2.66	3.14	$n=8$ .60	2.25	$n=8$ .28	9.4	$n=5$ 1.02	1.60	$n=5$ .04	1/4
EL60-40 Box A	60	+8	10.27	3.13	2.73	-	-	-	26.37	$n=5$ .98	3.30	$n=5$ .06	1/8
EL60-40 Box A	60	+8	13.76	2.90	2.68	$n=6$ .71	1.79	$n=6$ .13	22.16	$n=4$ 2.4	3.29	$n=4$ .08	1/4
EL60-40 Box C	60	+8	7.48	1.88	2.62	$n=6$ .38	1.00	$n=6$ .41	25.68	$n=4$ 1.5	3.09	$n=4$ .12	1/8
EL60-40 Box C	60	+8	10.97	2.28	1.61	$n=5$ .64	4.33	$n=5$ .29	23.30	$n=4$ 2.6	3.26	$n=4$ .18	1/4

## COMPARABLE LAMINATES

Sample Identification	Comp. Str. $\times 10^4$ PSI	95% CL Comp. Mod. $\times 10^6$ PSI	95% CL Flex. Str. $\times 10^3$ PSI	95% CL Flex. Mod. $\times 10^6$ PSI
ELR3-1	3.53 $\leftrightarrow$ 2.77	2.27 $\leftrightarrow$ 1.85	10.9 $\leftrightarrow$ 10.5	2.11 $\leftrightarrow$ 1.77
ELR3-6	1.62 $\leftrightarrow$ 1.06	2.30 $\leftrightarrow$ 1.80	13.0 $\leftrightarrow$ 7.0	1.91 $\leftrightarrow$ 1.59
ELR3-9	1.93 $\leftrightarrow$ 0.99	2.41 $\leftrightarrow$ 1.57	12.0 $\leftrightarrow$ 8.6	1.82 $\leftrightarrow$ 1.66
ELR3-12	2.80 $\leftrightarrow$ 2.68	3.71 $\leftrightarrow$ 2.11	15.9 $\leftrightarrow$ 9.9	2.03 $\leftrightarrow$ .89
ELR3-15A	3.23 $\leftrightarrow$ 2.25	2.28 $\leftrightarrow$ 1.44	12.7 $\leftrightarrow$ 8.9	1.79 $\leftrightarrow$ 1.65
ELR3-15B	3.64 $\leftrightarrow$ 2.64	2.31 $\leftrightarrow$ 1.91	10.7 $\leftrightarrow$ 8.1	1.65 $\leftrightarrow$ 1.55
EL60-40 Box A	-	-	27.6 $\leftrightarrow$ 25.2	3.4 $\leftrightarrow$ 3.2
EL60-40 Box A	2.92 $\leftrightarrow$ 2.44	1.91 $\leftrightarrow$ 1.75	26.0 $\leftrightarrow$ 18.3	3.42 $\leftrightarrow$ 3.16
EL60-40 Box C	3.02 $\leftrightarrow$ 2.22	2.41 $\leftrightarrow$ 1.57	28.2 $\leftrightarrow$ 22.3	3.28 $\leftrightarrow$ 2.90
EL60-40 Box C	2.20 $\leftrightarrow$ 0.62	2.63 $\leftrightarrow$ 1.97	27.4 $\leftrightarrow$ 19.2	3.55 $\leftrightarrow$ 2.97

Table 61

Molding Parameters for Laminates in Table 60

<u>Sample Ident.</u>	<u>Cal.</u>	<u>"B" Staged</u>	<u>Pre-Heat</u>	<u>Cont. Pres.</u>	<u>Contact Temp.</u>	<u>Contact Time</u>	<u>Molding Pres.</u>	<u>Molding Temp.</u>	<u>Molding Time</u>
ELR 3-1	Yes	Yes	-	-	-	-	2500 lb.	250°F	30 mins.
ELR 3-6	Yes	Yes	40 sec.	-	-	-	2500 lb.	250°F	30 mins.
ELR 3-9	Yes	Yes	35 sec.	0	250°F	1 min.	2500 lb.	250°F	30 mins.
ELR 3-12	Yes	No	-	0	250°F	11 min.	2500 lb.	250°F	30 mins.
ELR 3-15A	Yes	Partial	25 sec.	0	250°F	6 min.	2500 lb.	250°F	30 mins.
ELR 3-15B	Yes	Yes	25 sec.	0	250°F	6 min.	2500 lb.	250°F	30 mins.
EL 60-40 Box A	Yes	Yes	-	0	300°F	3 min.	2500 lb.	300°F	30 mins.
EL 60-40 Box A	Yes	Yes	-	0	300°F	3 min.	2500 lb.	300°F	30 mins.
EL 60-40 Box C	Yes	Yes	-	0	300°F	3 min.	2500 lb.	300°F	30 mins.
EL 60-40 Box C	Yes	Yes	-	0	300°F	3 min.	2500 lb.	300°F	30 mins.

Resin system used in above: JD 509 Shell Z

Note: "B" staged material was dielectrically heated and recalcandered before molding.

Laminates ELR3-6, ELR3-9 and ELR3-12 were prepared to determine the effect of layering plies of oriented sheets to form laminates upon physical properties and effect recalendering has upon the laminates.

Laminate ELR3-6 was reprocessed through the roller calender using the same nip clearance used in the first pass through. The sheet size increased and bead buildup on the feed sides of the rolls were noticed, indicating substantial decompression had been experienced after the first pass.

In preparing laminate ELR3-9, the parting film was removed from one surface of two squares of the wet sheet. The two sheets were pressed together by hand to form a single sheet.

Laminate ELR3-12 was prepared by removing the parting paper from both sides of two sheets of wet premix. The two sheets were molded immediately.

Examination of the data in Table 60 shows that wet molding of the oriented glass flake sheet material produced the strongest laminate. Except for tensile properties, no difference between the recalendered sheet and the hand bonded 2-ply laminate was found. The recalendered sheet showed some improvement in tensile properties. This increase results from an increased flake orientation.

The EL60-40 Box A and EL60-40 Box B laminate series was prepared in an attempt to determine if classified flake selected from boxes which contained wide difference in size distribution would produce laminates possessing different properties. Theoretically, if only the flake size was different, classification of flake should eliminate this variable and produce laminates with similar properties.

The blending, processing and molding of the four laminates were performed under rigid controlled procedures (Table 63). The laminates were prepared in two thicknesses and exhibited no visual differences which were readily apparent.

Examination of Table 60 shows that both laminates produced from glass identified as Box A exhibited significantly higher compressive properties than those produced from Box C. While confidence limits were not determined, average tensile values indicate similar trends exist.

The unclassified glass flake in Box A contained substantially less of the large size flakes than did Box C. Therefore, we had to conclude classification of flakes from dissimilar original lots does not produce similar laminate properties.

The laminates in series ELR3-1, ELR3-15A and ELR3-15B (Table 60) were prepared to evaluate the effect of vacuum blending upon physical properties and the effect of variation in the extent of the partially cured resin (B-stage) upon physical properties.

The blending, processing and molding of the laminate specimens was rigidly controlled (Table 61). The vacuum hopper Abbe blending process is fully described elsewhere in this report.

Examination of Table 60 shows no trends even though the average tensile strength of the vacuum hopper blends appears to be higher. The molding and roller-calendering processing of all three of the laminates was identical. Therefore, since the glass flake size distribution of the final premix was the same in all cases, the similarity in physical properties of the laminates is understandable. The glass flake breakdown studies have shown that glass flake pre-mixes which have been Abbe blended exhibit similar glass flake size distribution regardless of the premix blending process used.

#### IV.3.5.5.2.1. Conclusions

Increased physical properties are obtained when roller-calendered sheet material is laminated. Tensile strength appeared unaffected by glass flake content. An apparent variation in the chemical composition was uncovered in the last order of flake purchased. These flakes exhibit a marked solubility in concentrated nitric acid. The effect of this chemical difference upon such important factors as resin to glass flake bonding, untreated glass flake physical properties and glass flake laminate properties is unknown. The result obtained with laminates from an anhydride cured epoxy system which had yielded the highest tensile value obtained during the contract period was not reproduced when fabricated from a new batch of flake.

Molding "wet" oriented sheets produces laminates which are stronger than layering B-stage plies or layering wet sheet and B-staging the composite before molding. Recalendered sheet produced laminates with properties similar to properties obtained from specimens in which sheet was calendered only once. This indicates that use of a calender with additional roller units could compress and orient the flakes further to produce superior laminates.

Classification of dissimilar glass flake lots does not produce a common base material. This information increases our belief that each lot of glass flakes is possibly chemically and physically different, will cause unpredictable process variability and may result in unforeseen strength variations.

Vacuum processing of resin glass mixtures increased tensile properties of the laminates slightly. The degradation of glass flakes during the blending process under vacuum causes a reduction of the glass flake particle size to a level similar to that obtained when blending occurs at atmospheric pressure.

#### IV.3.5.5.3. Micro Appearance of Glass Flake

In addition to determining the glass flake content, breakdown in size distribution, effect of distribution on processing upon laminate properties and orientation on physicals, the micro appearance of glass flakes in laminates was determined.

Photomicrographs were obtained on selected specimens ranging from 50% to 80% glass flake contents. Table 62 lists the process and molding parameters of the laminates from which the photographed specimens were chosen.

#### Analysis of microphotographs

Photomicrographs were made of the following laminates:

EL-15-18	70% glass
EL-15-20	50% glass (20 tons molding pressure)
EL-15-21	60% glass (15 tons molding pressure)
EL-15-22	60% glass
EL-15-34	80% glass
EL-23-4	70% glass

At the 50% and 60% glass content (EL-15-20 and -21 cf. Photographs 33 and 34) flake alignment within the composite appears quite uniform with some instances of curved flakes. Resin binder thickness appears to be on the order of 8-15 microns thick. This minimum resin binder thickness has been postulated as a key factor in tensile strength properties. We believe the desirable resin binder thicknesses have resulted from the use of high pressures on the preformed sheets during curing. In Photograph 33 the transverse cross-section illustrates the presence of a thicker resin boundary where the two preforms bonded. ~~Some smaller flakes probably resulting from crushing during bonding, and a departure from flake parallelism. It is believed that the~~ slightly larger resin binder thickness observed has no effect on laminate tensile properties because it is still less than 20 microns. Previous work indicates that a thickness of 20 microns and greater in resin binder will lower strength properties.

Photograph 34 illustrates a 60% glass laminate (EL-15-21) molded at a pressure of 15 tons. Photograph 33 illustrates a 50% glass laminate molded at 20 tons hydraulic pressure. The laminates had average tensile strength values of 14.1 and 14.0 respectively. Flake spacing in the laminate produced at the lower pressure appears slightly larger but still within the range believed desirable.

Photograph 35 depicts the EL-15-22 laminate containing 60% glass. The tensile strength of this sample was unexpectedly low, 10,800 psi. The microphotograph of this specimen contains a possible explanation for this result. At the center of the laminate, where the two preforms used are bonded, there appears to be an area where large resin binder thickness is significantly greater than in other pictures. At one point, resin binder thickness is 32 microns. Orientation of the flake throughout the remainder of the composite appears uniform and average resin binder thickness varies from 2-12 microns. The resin binder thickness of the 60% glass sample is lower than the resin binder thickness of the 50% glass laminate as would be expected from higher glass content.

TABLE 42  
LAMINATES CHOSEN FOR PHOTOMICROGRAPH STUDY

Photograph Number	Laminate Number	% Glass	Method of Fabrication	Forming		No. of Preforms	Molding		Time Mins.		
				Temp. Of	Pressure		Temp. Of	Pressure			
33	EL-15-20	50	Dry blend	170	250	2	220	1.5	220-370	30 tons	45
34	EL-15-21	60	Dry blend	170	250	1	220	1.5	220-370	15 tons	45
35	EL-15-22	60	Dry blend	170	250	2	220	1.5	220-370	30 tons	45
36	EL-15-18	70	Dry blend	220	C	2	220	.5	220-370	30 tons	45
37	EL-15-34	80	Dry blend	160	200	2	270	1.5	270	30 tons	35
38	EL-23-4	70	Wet premix	-	-	-	200	10	200	250 psi	2 hrs





Photograph 33

Photomicrograph (100 X) of Laminate EL-15-20  
containing 50 per cent glass

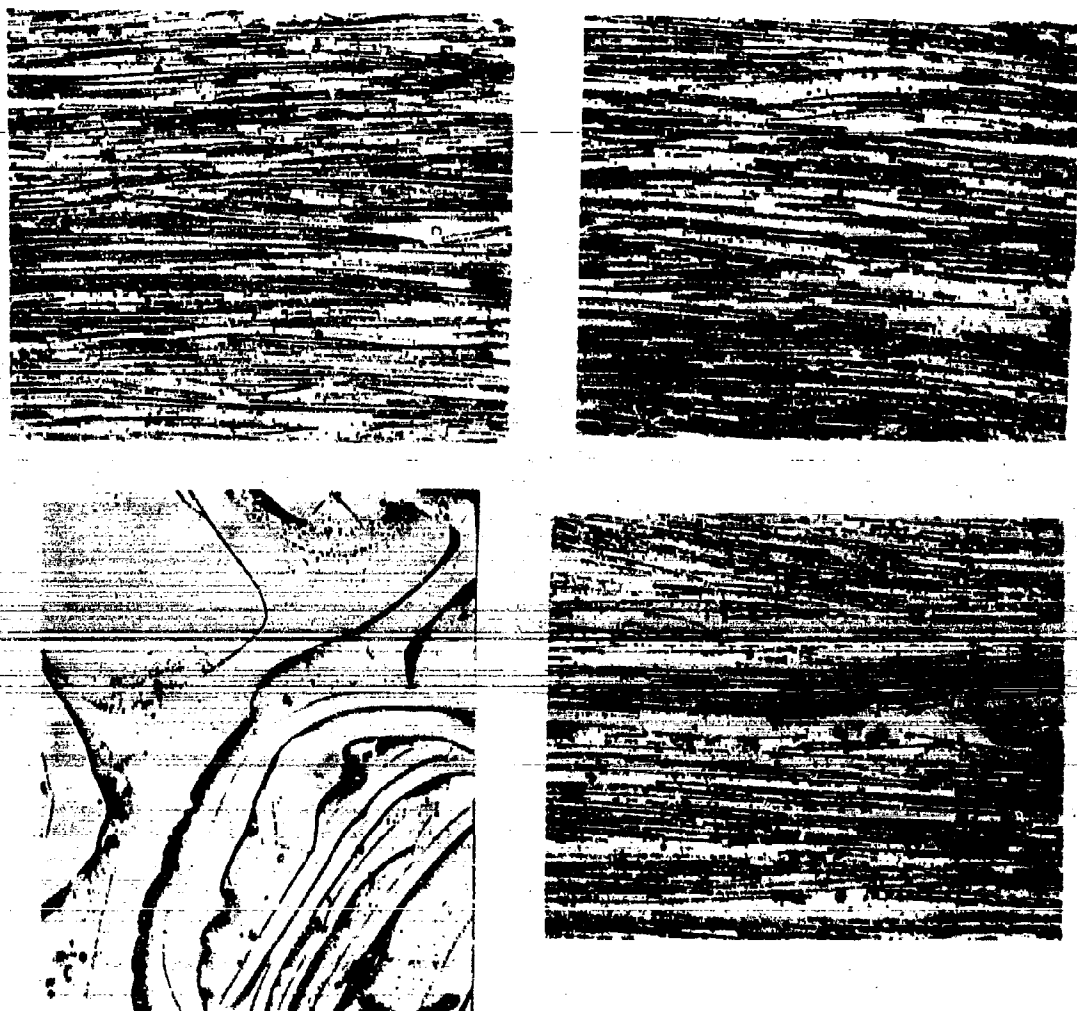
UL: average appearance  
UR: longitudinal cross section  
LL: surface perpendicular to lamination  
LR: transverse cross section



Photograph 34

Photomicrograph (100 X) of Laminate EL-15-21  
containing 60 per cent glass

TOP: surface perpendicular to lamination  
LL: longitudinal cross section  
LR: transverse cross section



Photograph 35

Photomicrograph (100 X) of Laminate EL-15-22  
containing 60 per cent glass

UL: average appearance  
UR: longitudinal cross section  
LL: surface perpendicular to lamination  
LR: transverse cross section

The 70% glass laminate, EL-15-18, Photograph 36, exhibited good flake orientation and smaller resin binder thickness approximately 1 to 4 microns. Correspondingly, the average tensile strength of this laminate was high, 15,300 psi, and again, the appearance of a resin rich bond line is revealed where the two preforms were joined. This resin rich line is only approximately 20 microns in thickness.

The 80% glass content laminate, EL-15-34, Photograph 37, reveals an even closer glass flake packing, with an average resin binder thickness of 1 to 3 microns. This close flake packing would account for the high average tensile moduli of 9.63 million psi reported. Many flakes seem to have no resin between them, indicating that resin coverage is sparse. This observation coupled with the recorded low tensile strength value of 13,200 psi is indicative that a limiting glass content is being approached where insufficient resin coverage contributes to reduction of tensile strength properties.

Photograph 38 shows, for comparison, a laminate containing 70% glass prepared by the Abbe mixing method, which utilizes liquid resin blending. This laminate, EL-23-4, is the same laminate that has exhibited tensile strength found in this program, 22,900 psi (average 19,600 psi). The uniform flake parallelism, and low resin binder thickness (1-3 microns) are obvious. The picture, in support of flake orientation and resin thickness theory demonstrate the advantages Abbe premixes have apparently in yielding laminates having higher tensile strength, tensile moduli, flexural strength and flexural moduli.

#### IV.3.5.5.3.1. Conclusions

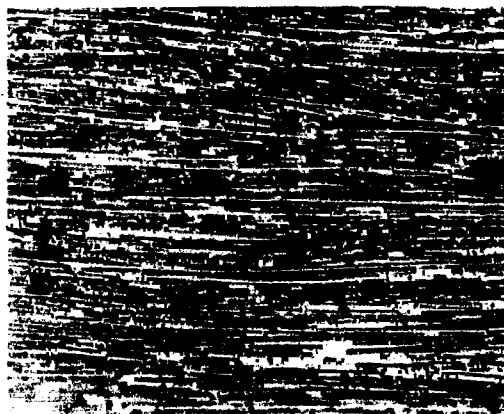
Maximum resin binder thickness should not exceed 20 microns. Preform sheets exhibit thicker inter-sheet resin layers but generally the thickness is below the 20 micron range. Compression molding pressure adversely affects glass flake size. Eighty per cent glass flake content laminates exhibit micro-resin starved areas indicating an approach to maximum glass loading content.



Photograph 36

Photomicrograph (100 X) of Laminate EL-15-18  
containing 70 per cent glass

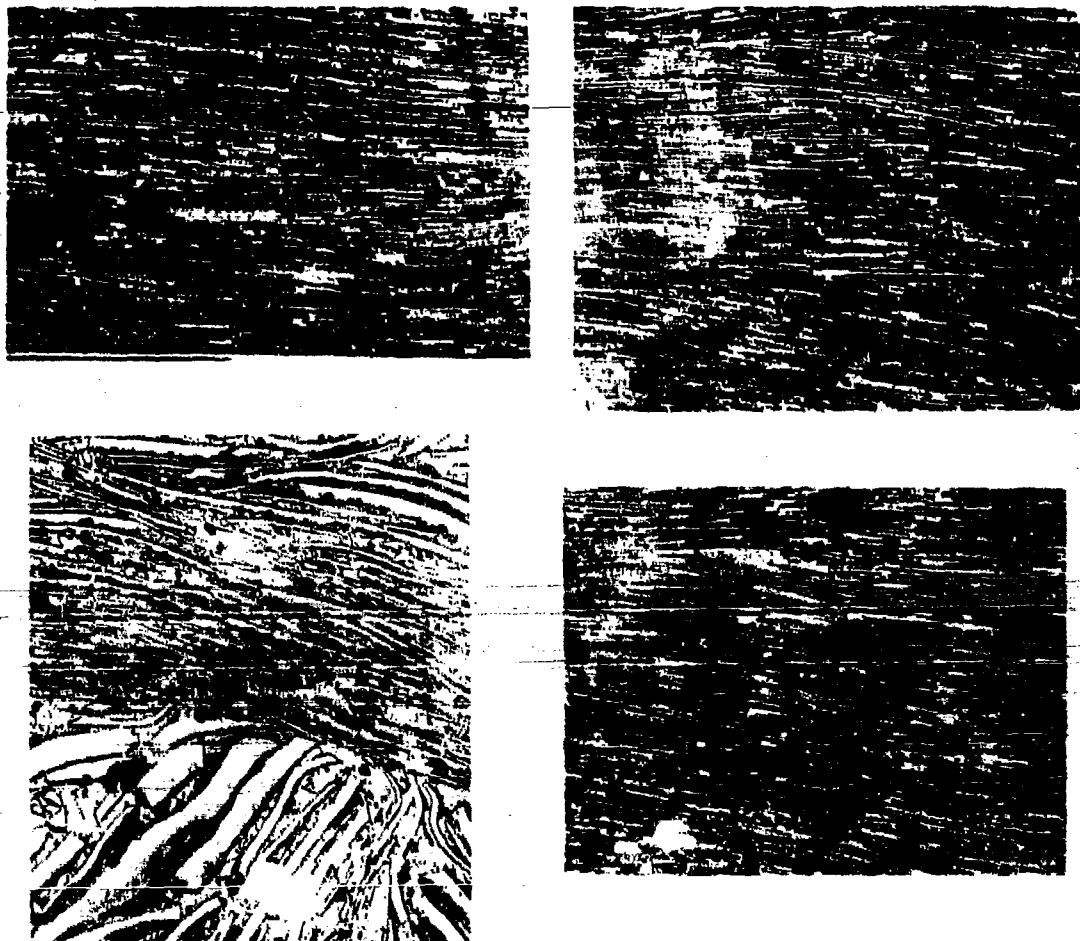
UL: average appearance  
UR: longitudinal cross section  
LL: surface perpendicular to lamination  
LR: transverse cross section



Photograph 37

Photomicrograph (100 X) of Laminate EL-15-34  
containing 80 per cent glass

UL: average appearance  
UR: longitudinal cross section  
LL: surface perpendicular to lamination  
LR: transverse cross section



Photograph 38

Photomicrograph (100 X) of Laminate EL-23-4  
containing 70 per cent glass

UL: average appearance  
UR: longitudinal cross section  
LL: surface perpendicular to lamination  
LR: transverse cross section

## V. Phase III Fabrication of Selected Complex Shapes

### V. 1. Introduction

After approximately a year of effort devoted to selection of resin systems from commercially available supply, the development of mixing methods, and the pilot studies of process capability, a decision was made to begin Phase III of the study. We recognized the limitations of the systems developed to that time, but believed it to be in the best interests of the Air Force to initiate the investigation of the capabilities of glass flake resin premixes in conventional plastics production facilities. Concurrent with this, we continued to work additional theory and leads on Phase II.

Although the contract permitted the expenditure of several thousand dollars for dies, molds and related equipment, we felt that sufficient aircraft and missile parts were being produced from reinforced plastics to permit us to negotiate with other Air Force contractors for use of their facilities. This approach would not only save the Air Force money, but would also present an opportunity to evaluate glass flake resin systems in direct comparison with standard production plastics missile hardware. We were gratified with the acceptance and speedy approval by the sponsor of this concept, and promptly began a survey of Air Force contractors in this geographical area where Phase III might be performed under our technical cognizance.

A subcontract for the production prototype molding of Phase III with the Plastics Division of Raytheon Manufacturing Company in Maynard, Massachusetts, was approved by the sponsor. The Plastics Division of Raytheon specializes in the molding of reinforced plastics and composites for the military. They have molded radomes, nose cones and rocket nozzles, etc. and were equipped with the necessary molds, high pressure presses, and other plastics fabrication equipment to fully evaluate our approaches to Phase III molding. The following were compression molded:

1. Missile fin
2. Practice nose cone
3. An ablative test nose cone
4. Nose cone insert
5. Rocket exhaust nozzle

A sixth and seventh configuration, the Electronic Gate and Electronic Bridge were transfer molded. The seventh configuration was molded at IBM, Peekskill, New York.

### V. 2. Missile Stabilizing Fin

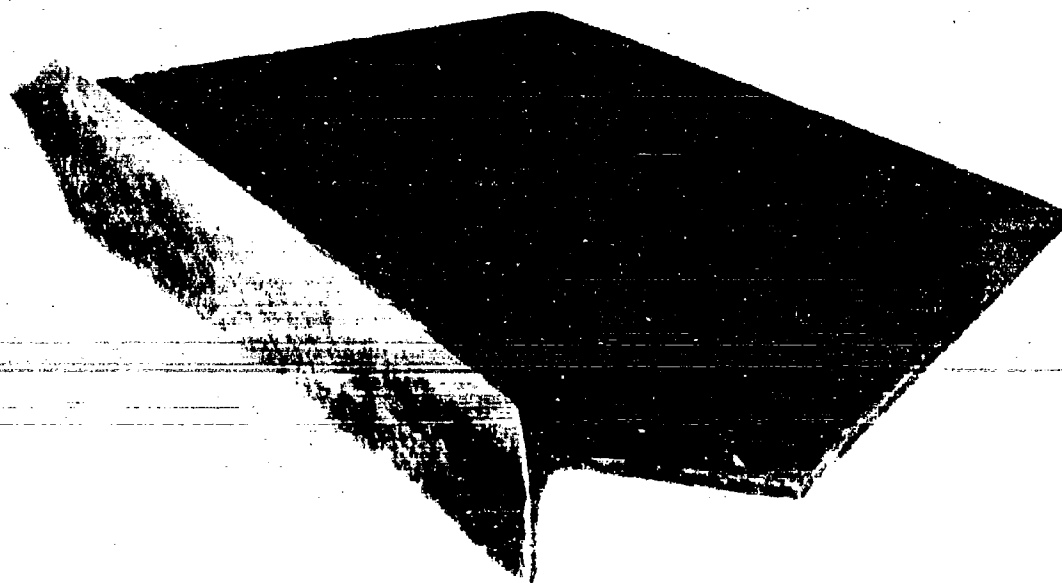
#### V. 2.1. 50% Glass Content (Epoxy Resin System)

Photographs 39, 40 and 41 show the molded fin. To mold these fins, the B-staged granulated dry epoxy premix containing 50% glass flake was used. Using Raytheon's 7KW "Thermal" dielectric





Photograph 39  
Missile Fin  
50 Per cent Glass Flake-Epoxy Laminate



Photograph 40  
Side View of Missile Fin  
(showing detail of support base and fin  
as molded in press)  
50 per cent Glass Flake-Epoxy Laminate



Photograph 41  
Backlighted Missile Fin  
50 per cent Glass Flake-Epoxy Laminate

heater, we were able to dielectrically preform the molding compound into briquettes, 3-1/4 x 3-1/4 x 3/4 inch thick, which were subsequently preheated in the dielectric heater and molded in the six cavity mold. A total of 10 fins was made by this method. The first four fins were made at varying molding temperatures to see whether these flow lines, apparent in Photograph 41, could be reduced by using varied mold temperatures. It seemed apparent that the number of the flow lines could be reduced, but not completely eliminated by manipulation of molding temperature. A range of 270-300°F. resulted in the least number of flow lines in the molded fin.

Excellent mold fill and mold reproducibility was exhibited by the epoxy-glass flake system. The molding of the resin-glass composite into the fin shape was made difficult because of flow requirements to fill the mold. The resin must flow along a horizontal plane and then into a vertical "T" section within the mold. The support base of the fin is molded in this fashion. The fins are molded in a six cavity mold in the position indicated in Photograph 40. (The fins pictured in Photographs 39 and 40 exhibit some streaking on the surface. This is caused by an excess of mold release, Garan 225, mixing with the premix charge.)

#### V. 2.2. 70% Glass Content (Epoxy Resin System)

A series of fins was also molded containing 70% glass flake reinforcement and the same epoxy resin system used for the fins molded with 50% glass as above. The molded appearance of the fins containing 70% glass was much improved. The fins produced containing 50% glass flake with respect to the presence of point lines within the laminate.

In molding the 70% glass missile fins, it was discovered that the B-staged dry premix could also be preformed using a 7KW dielectric heater followed by compression into the 3-1/4 x 3-1/4 inch briquette. However, it was also discovered that the amount of preheating required to enable the premix blend to be preformed (80 seconds) advanced the cure of the resin binder system so that during molding, the resin did not flow sufficiently to give a translucent part.

The method used to mold the fin with the best molded appearance was to preheat the dry premix for 10 second and then bulk load the material into the mold.

#### V. 2.3. 70% Glass Content (Polyester Resin System)

The polyester resin based premixes which cannot be B-staged or preformed, are charged directly into the fin mold. Molded appearance of these fins was acceptable, however, only two of the eight molded fins could be ejected from the mold without breaking. Poor hot-strength of the polyester laminates was responsible for these failures.

Table 63 presents the summary of preforming and molding parameters used in the molding of the nose cone inserts and missile fins.

The fins produced with the 50% and 70% glass-epoxy molding compounds were cut for testing of the tensile and flexural strengths. These properties were then compared with those of the fin being molded by Raytheon with Minnesota Mining and Manufacturing's fiberglass reinforced molding compound "Scotchply 1100". The comparative data presented in Table 64 indicate that both the tensile and flexural strength of the glass flake reinforced missile fin are substantially lower than the fiberglass reinforced fin, as experienced in previous comparisons of the two systems. However, it should be noted that the tensile moduli are equivalent in the molded fins. Of importance is the greater flexural modulus attainable with the 70% glass flake reinforced fin; which is twice the flexural modulus of the fiberglass reinforced fin.

#### V. 2.4. Miscellaneous Molded Fins

Four fins were also molded from a B-staged premix containing a phenolic resin binder, however, none of these were blister-free. The silicone resin system was not used because of the long curing time.

The general molding procedure used was identical for all the other parts molded. A 200-225 gram charge was placed in the pre-heated compression mold and cured as indicated in Table 65.

Photograph 42 illustrates seven of the molded fins. Three contain 50% glass flake - the remaining contain 70% glass flake. Also, a fin containing 80% glass flake was molded which was poor. Resin flow during molding prevented complete bonding of the support base to the vertical fin section although molded appearance of the fin section was excellent.

Photographs 43 and 44 illustrate four of the inert filled missile fins formulated with polyester resin, glass flake, asbestos and calcium carbonate.

#### V. 3. Nose Cone Insert

Photographs of the molded parts appear in Photographs 45, 46, 47 and 48. Photographs 45 and 46 depict the front and rear views of the 7" diameter convex part. The mold used was a semi-positive mold with the male cavity located in the bottom platen and the female cavity located in the upper platen of the press. This arrangement is used in order to mold in a special wet lay-up and two copper inserts. (Ordinarily, with other compression molds, the male cavity is located in the upper platen of the press and the female cavity is located in the lower platen of the press.)

Table 63  
Molding Parameters for Missile Fin and Nose Cone Insert

Item	P <sub>o</sub>	Material Form	M <sub>ph</sub>	M <sub>p</sub>	M <sub>o</sub>	M <sub>t</sub>	Molded Parts
Nose Cone Insert	None	Wet Epoxy Premix 50% Glass	0	1570 psi	20	270	1
		Wet Epoxy Premix 50% Glass	0	260 psi <sup>*</sup> 1570 psi	20	270	1
		B-staged Epoxy Pre-oriented sheets--50% glass	0	260 psi	10	270	1 Best appearance
Missile Fin	50	Pulverized B-staged 50% glass	30	4000	12	270-300	2
	50	" "	50	4000	16	270-300	2 Best appearance fins
	50	" "	35	1600	16	220-250	6
Missile Fin	80	70% Glass 30% Epoxy B-staged	50	4000	16	270-300	6
	80	" "	10	4000	16	270-300	6
	None	" "	10	4000	16	250-270	4
None	None	70% glass 30% Polyester	Bulk Loaded	2000	8	200-210	4
	None	" "		2000	8	200-210	4

\*press closed under 260 psi pressure-then increased to 1,770 psi

Supplement to Table 63**Preforming:**

$P_{\theta}$  = preheat time in "Thermal" 7KW Dielectric heater, seconds

**Preheating prior to molding:**

$M_{ph}$  = preheat time in "Thermal" 7KW Dielectric heater, seconds

**Molding Parameters:**

$M_p$  = molding pressure on Fin, psi

$M_{\theta}$  = molding time, minutes

$M_t$  = molding temperatures, °F.

**Molding equipment used at Raytheon:**

Insert: 30 ton Elmes Automat. "Hydrolair" Press

Fin: 460 ton Erie Engine & Machine Co. Compression Press

**Formulations:****Parts**

Epoxy: Jones Dabney 509  
" " 504

75  
25

Shell 2  
(Eutectic amine mixture)

Polyester: American Cyanamid

Laminac 4128  
Benzoyl peroxide

100  
2

**Mixing:**

1/2 hr. in Abbe mixer at 45 rpm.

Table 64

**Comparative Tensile and Flexural Strengths of Missile Fin -  
Glass Flake and Fiberglass Reinforced**

Reinforcement	% Glass	Average Tensile		Average Flexural	
		Strength	Modulus	Strength	Modulus
Glass Flake	50	4690 psi	$1.5 \times 10^6$ psi	15,800 psi	$1.8 \times 10^6$ psi
" "	70	5420 psi	$1.7 \times 10^6$ psi	17,500 psi	$4.1 \times 10^6$ psi
Fiberglass* (1/2 in. strands)	65	24,000 psi	$1.75 \times 10^6$ psi	55,400 psi	$1.8 \times 10^6$ psi

\*As present in Minnesota Mining & Manufacturing Company's molding compound "Skotch Ply 1100"



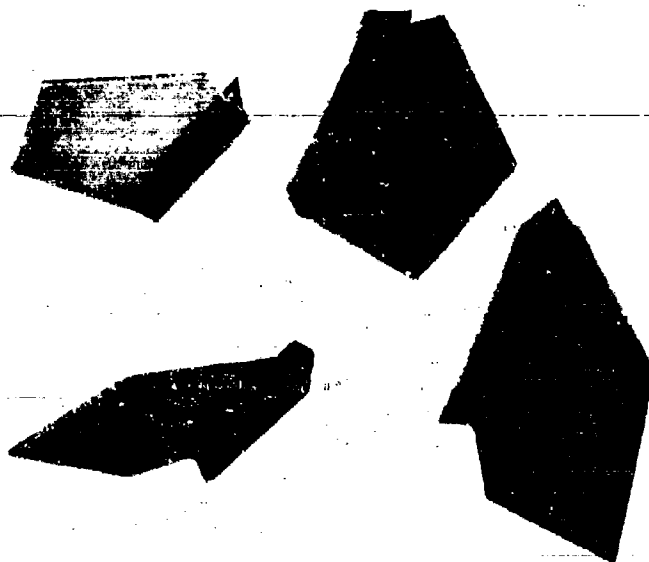
TABLE 65

**Formulations & Molding Variables for Glass Flake  
Reinforced Missile Stabilizing Fins**

	Parts 1 - 3 Photo 42 Epoxy Binder	Parts 4 - 7 Photo 42 Epoxy Binder	Not Shown Epoxy	Photo 44 Polyester	Photo 43 Filled Polyester
Preforming Time, Seconds	50	-	-	-	-
Preheating Time, Seconds	50	10	-	-	-
Molding Temperature, °F.	275	275	275	210	250
Molding Pressure, psi	1600	4000	4000	2000	1000
Molding Time, Minutes	16	16	16	8	8
Formulation: Parts					
Jones Dabney Epi-Rez 509	75	75	75	-	-
Jones Dabney Epi-Rez 504	25	25	25	-	-
Shell Curing Agent Z	20	20	20	-	-
American Cyanamid : minac 4128	-	-	-	100	100
Benzoyl Peroxide	-	-	-	2	2
Fillers:					
Glass Flake, Wt. %	50	70	80	70	25
Asbestos 7TF	-	-	-	-	10
Surfex MM-Calcium Carbonate	-	-	-	-	20
Resin Content, Wt. %	50	30	20	30	45

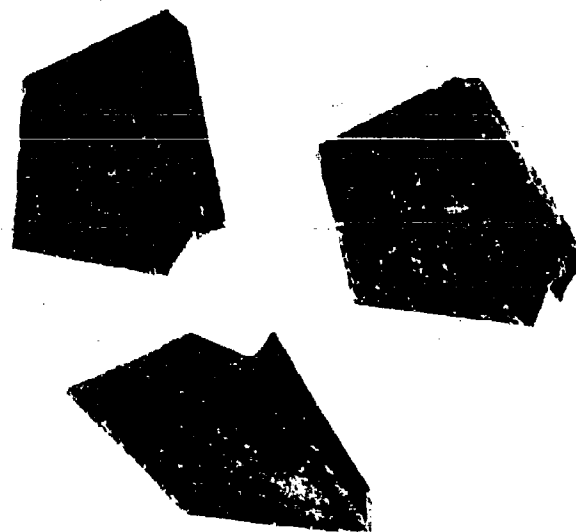
**NOTES:**

All epoxy fins molded from B-staged material  
Polyester premixes bulk loaded  
Fins molded in 6-cavity or 2-cavity mold  
460 Ton Emco press  
7 1/2 kw "Thermal" dielectric heater used for preforming & preheating



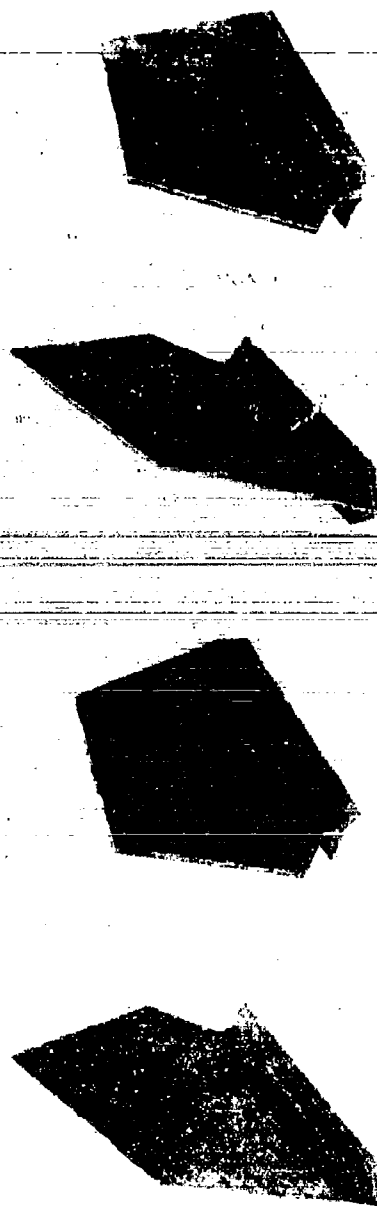
Photograph 42  
Missile Stabilizing Fins Glass Flake Reinforced - Epoxy Binders

Right  
4 Fins  
reinforced with  
70% glass flake



Left  
3 Fins  
reinforced with  
50% glass flake

Refer to Table 65 for formulation and curing data



Photograph 43

Missile Stabilizing Fins

Glass Flake Reinforced Polyester Binder and Inert Filler



Photograph 44  
Missile Stabilizing Fin  
70 Per Cent Glass Flake Content  
30 Per Cent Polyester Resin Binder

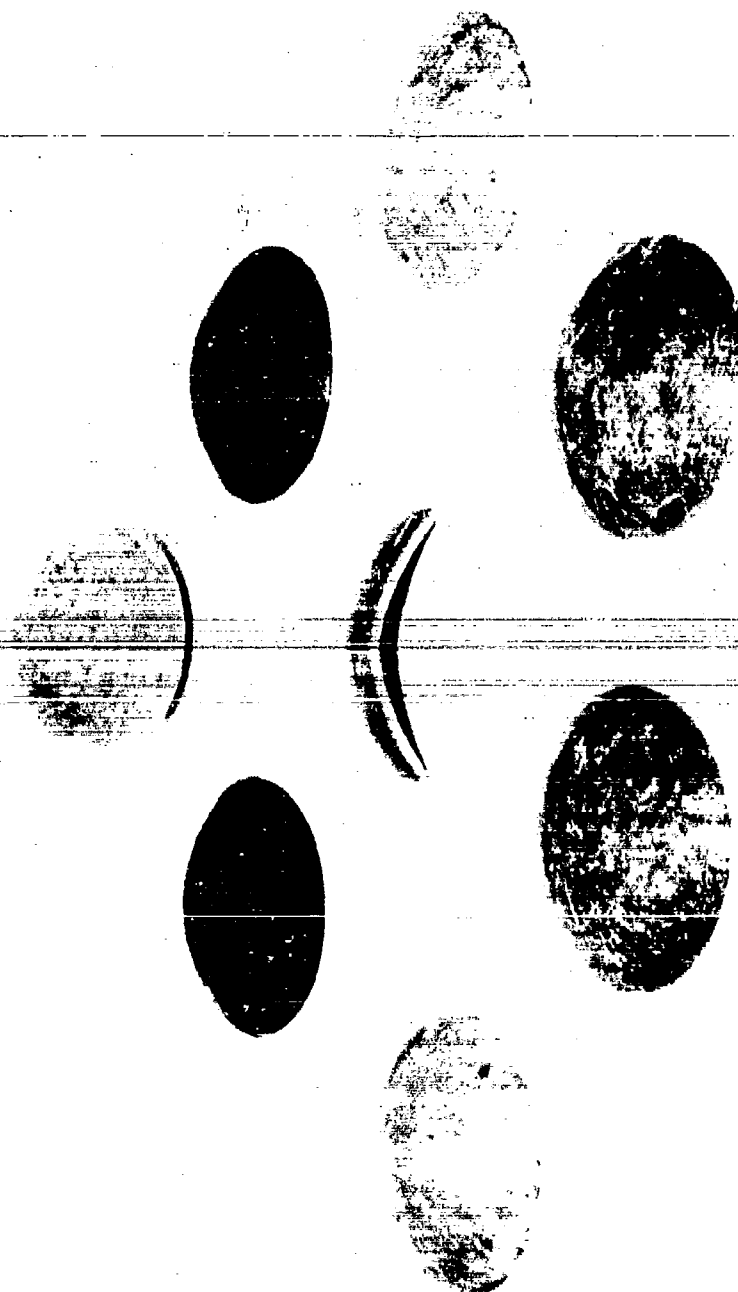


Photograph 45  
Front View of 50 Per Cent Glass Flake-Epoxy  
Nose Cone Insert  
(Convex Surface)



Photograph 46  
Rear View of 50 Per Cent Glass Flake-Epoxy  
Nose Cone Insert  
(Concave Surface)

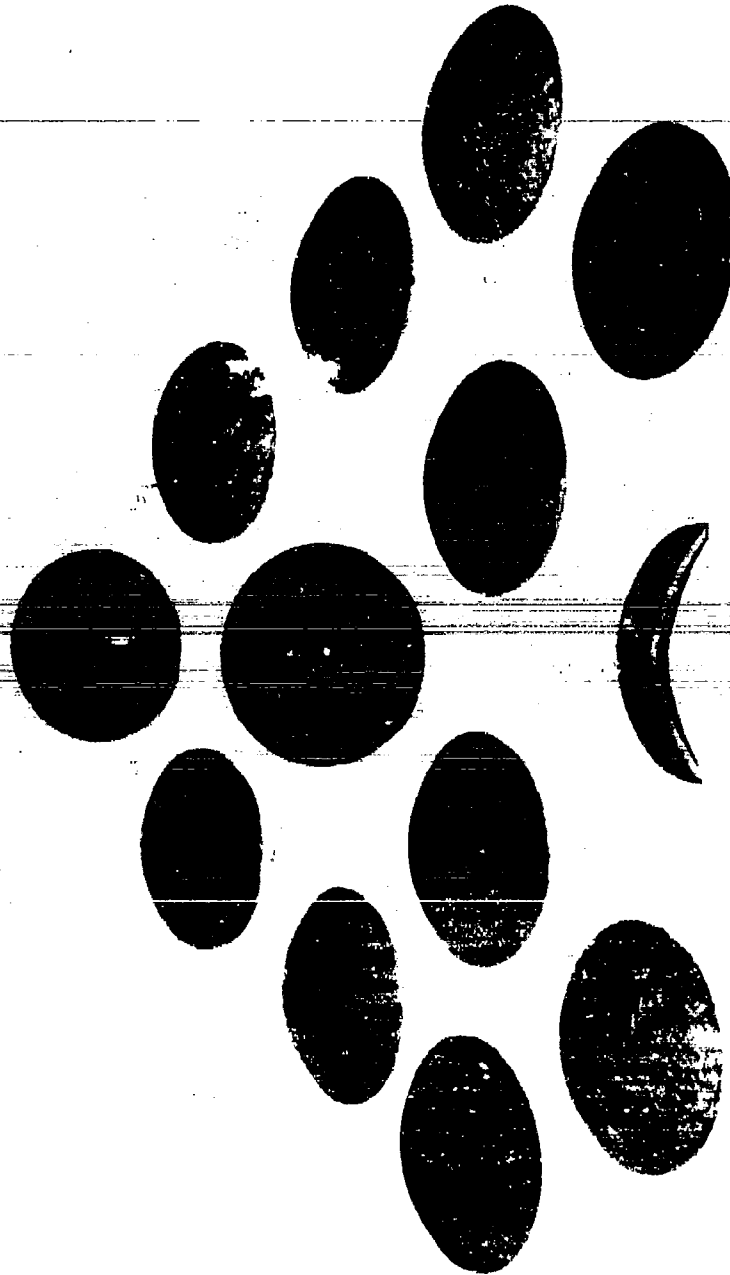
Photograph 47  
Nose Cone Inserts Reinforced with 50% Glass Flake



<u>Part #6</u> Polyester Binder		<u>Part #1</u> Polyester Binder		<u>Part #3</u> Polyester Binder	
<u>Part #7</u> Epoxy Binder		<u>Part #2</u> Epoxy Binder		<u>Part #4</u> Epoxy Binder	
<u>Part #5</u> Epoxy Binder		<u>Part #1</u> Polyester Binder (Cross Section)		<u>Part #4</u> Silicone Binder Insert Not Shown	

See Table 66 for Curing and Formulation Data

Photograph 48  
Nose Cone Inserts Prepared With & Without Inert Fillers



Part #G	Part #B	Part #A	Part #C	Part #F	Part #J
Part #D	Part #H	Part #E	Part #I	Part #L	
Part #K			(Cross Section)		



This part is later molded into the head of a tactical nose cone. The molded part weighs 300-350 grams and the production unit is molded from a polyester-fiberglass reinforced premix molding compound containing inert fillers.

The characteristics of the mold required that we formulate a premix capable of being formed into a ball and placed upon the male cavity in the press. Dry molding compounds could not be used.

#### V. 3.1. Description of the Molding Procedure

A preweighed premix charge of 400-450 grams is formed into a ball by hand and then placed at the apex of the male mold. The press is then closed and curing takes place in accordance with the prescribed cycle. The formulations and curing parameters for the inserts are presented in Table 66.

The method described previously was used to fabricate inserts from a 50% glass-50% epoxy resin wet premix. Parameters for units molded by this technique are recorded in Tables 63 and 66.

The alternative method used to make one piece was to place several preoriented B-staged sheets of 50% glass, epoxy based on the male cavity and close the mold. The latter method, although more troublesome with respect to handling operations, yielded the best of three parts. Replication of mold surface and finish appeared excellent.

#### V. 4. Practice Nose Cone

Dimensions of this molded part are 11-1/2 inch length, 11 inch outside diameter by an approximate 0.250 wall thickness. The molded part weighs between six and seven pounds.

Production orders for this part are fabricated from a polyester resin binder reinforced with a chopped glass roving and modified with inert fillers. Compression molding is performed in a 460 ton press (Erie Engine and Machine Company). A single, steam heated cavity of a hardened, chrome plate steel is used.

These pieces were not made to obtain physical properties, but to show what molding conditions and techniques were required to yield a uniform product, eliminate flow knit lines, resin segregation by pressure flow, glass clumping and booking.

Tests of this nature are all evaluated visually and no physical tests of the pieces were made. Nose cones must be tested in a high temperature gas stream. This type of facility is not available so such tests were not made. Physical tests were not made on these pieces since they should be made in environmental equipment, which results in partial destruction of these pieces. Since additional pieces are not made specifically for testing and since the prime purpose was to demonstrate the molding technique, physical tests were not obtained.

#### V. 4.1. Description of the Molding Procedure

We concluded that plasticity of the molding formulation would be critical in the successful use of a glass flake premix in this mold. During molding of the part, the charged premix molding compound was forced to flow from the hemispherical section of the mold in an upward pattern to form a cylindrical wall. Our experience with the plasticity and flow values of glass flake premixes indicated that 50% to 65% glass flake content would be appropriate. The 70% glass premix would have been too "stiff" to obtain proper flow. Prior commitments for this mold limited our program to the production of five parts. One nose cone was formulated with a calcium carbonate filler added to control resin flow; the other four were formulated from resin and glass flake exclusively.

The procedures used for all five nose cones depicted in Photograph 49 were similar except for curing times. The molding conditions are tabulated in Table 67. In all cases, the weighed premix charge, 3000 grams, was charged into the preheated mold. After the recommended curing cycle, it was necessary to cool the mold to room temperature. Our trials showed that closing the press under the full pressure resulted in excess resin flow from the part and the appearance of resin-starved areas in the final part. These dry areas also produced mold sticking and several molded parts could not be removed without fracture. The application of a pressure of 200-250 tons to close appeared optimum for the resin formulation used.

#### V. 5. Test Ablative Nose Cones

This configuration as shown in Photograph 50 consists of a cone 3-1/2 " in diameter at the base and 3-3/4" over-all height. This nose cone is used to screen new plastic composites for ablation properties. The cone is solid but has a 1/2" diameter by 3/4" deep hole molded in the center of the base.

12/22/56

Formulation and Molding Variables for Glass Plates Reinforced Resin Core Inserts -  
(Epoxy, Polyester, & Silicone Binders - With & Without Inert Fillers)

	Part 41. 3/ 6 Photo 47 Polyester Binder	Part 42. 7 Photo 47 Epoxy Binder	Part 44. 5 Photo 47 Epoxy Binder	Not Shown	Part 45. 8 Photo 48 Polyester Binder	Part 46. 8 Photo 48 Epoxy Binder
Mold Temperature, °F.	230	270	200	300	230	200
Molding Pressure, psi	400	1570	400	200	400	600
Molding Time, Hrs.	10 min.	20 min.	1	3	10 min.	2
Post Cure	-	-	2	40	-	2
Time, Hrs.	-	-	400	250	-	400
Temperature, °F.	-	-	-	-	-	-
Formulation: Parts						
Jones-Dabney Epi-Res 509	-	75	100	-	-	100
Jones-Dabney Epi-Res 504	-	25	-	-	-	-
Methyl Radic Anhydride	-	-	96	-	-	95
DGP-10	-	-	2	-	-	2
Shell Curing Agent 2	-	20	-	-	-	-
American Cyanamid Laminac 4128	100	-	-	-	100	-
Benzoyl Peroxide	2	-	-	-	2	-
Dow Corning Silicone DC 7145	-	-	-	-	-	-
Di Cap N-Dicouyl Peroxide	-	-	-	100	-	-
Fillers:				3	-	-
Glass Flakes, %	50	50	56	50	25	25
Asbestos 777	-	-	-	-	15	15
Surfax 88-Calcium Carbonate	-	-	-	-	20	20
Resin Content, %	50	50	50	50	45	45

## NOTES:

1. All parts cooled below 150°F. before ejection from the mold.
2. Molding press: 30 Ton Elcom "Hydraulic"

### V. 5.1. Description of the Molding Procedure

The cone mold consisted of a three piece hand mold. After each cycle the mold was removed from the press and disassembled to recover the part.

A preweighed charge of 375 grams was used to mold each part. Molding data is presented in Table 68.

Flow patterns similar to those found in the nose cone and fin were evident in the finished ablative cone. Areas of resin rich or glass rich appearance attest to difficulties in controlling resin flow, a problem which must be resolved by formulation modification dependent upon die and mold design.

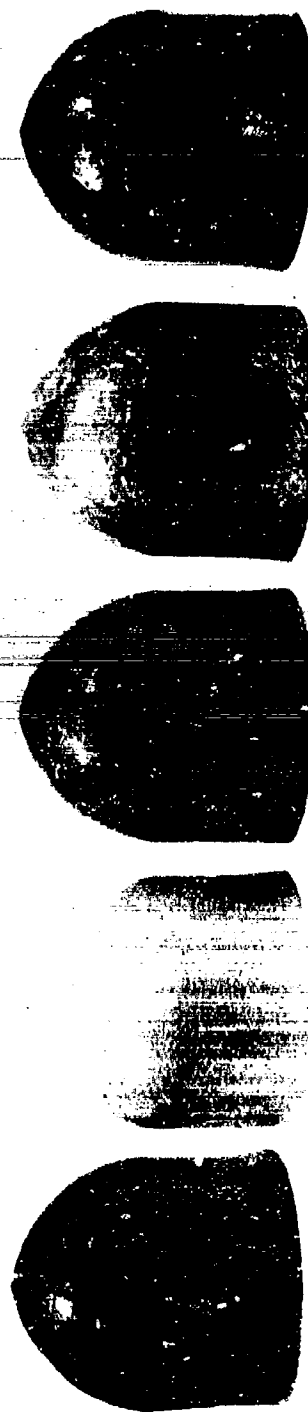
### V. 6. Rocket Exhaust Nozzle

The rocket exhaust nozzle is a truncated cone 2-1/2" high with base dimensions 3-3/4" O.D., 2-3/4" I.D. (1/2" walls), top dimensions 2-1/2" O.D., 1-1/2" I.D. (1/2" walls). The molded unit weighs approximately 275-300 grams and is molded in a match metal mold mounted in a 190 ton Emco (4.5" piston) compression press. A single steam heated cavity of hardened polished steel was used.

A new mold was installed the evening before the glass flake molding run was performed. Two units were fabricated with Scotchply 1100 (Minnesota Mining & Manufacturing Company reinforced premixed compound) the morning of the trial runs to establish some molding parameters with a commercial premix system.

### V. 6.1. Description of Molding Procedure

The female cavity is mounted on the bed of the Emco press and the male match metal portion on the movable compression bed. Wet B-staged resin-flake systems were molded as follows: the weighed premix charge was placed into the preheated mold cavity. The mold was closed rapidly until in contact with the glass flake-resin system then closed slowly (1-5 seconds) until fully seated. Cure times ranged from 5-24 minutes, the most effective range being 5-8 minutes. Molding temperatures ranged from 265-295°F. Molding pressures ranged from 15-70 p.s.i.



Photograph 49

Practice Nose Cones - Glass Flake Reinforced

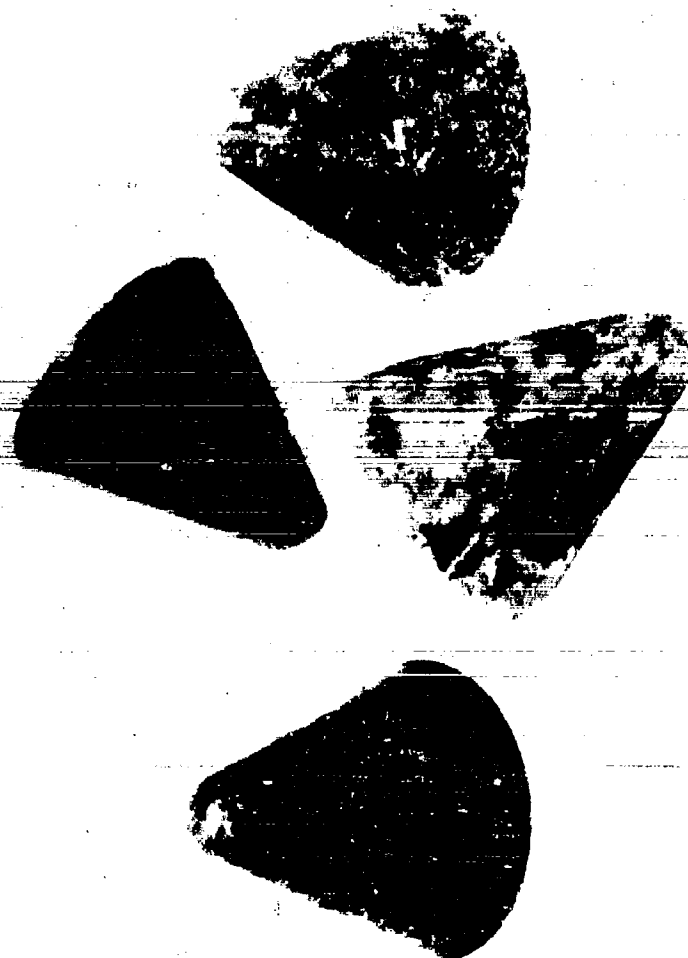
Part #1	Part #2	Part #3	Part #4	Part #5
60% Glass Flake Epoxy Binder Amine Cured	40% Glass Flake Inert Filler Anhydride Cured	Same as Part #1	50% Glass Flake Epoxy Binder Anhydride Cured	Same as Part #1

\*See Table 67 for Curing and Formulation Data

**TABLE 67**  
**Molding Parameters for Practice Nose Cone**  
**Formulated with Glass Flake Reinforced Epoxy Resin**

	Part 4 in Photo 49	Parts 1, 3, 5 in Photo 49	Part 2 in Photo 49
Mold Temperature, °F.	180	400	300
Molding Pressure, Tons	200	200	200
Molding Time, Hrs.	1	1	1
Step*	1	2	1
Formulation: Parts			
Jones Dabney Epi-Rez 509	100	75	100
Methyl Nadic Anhydride	95	-	95
Shell Curing Agent Z	-	220	-
Jones Dabney Epi-Rez 504	-	25	-
DMP-10	1.5	-	1.5
Resin Content, Wt. %	50	35	36
Fillers			
Glass Flake Content, Wt. %	50	65	40
Calcium Carbonate, Wt. %	-	-	24
(Surfex MM-Diamond Chemical Co.)			

\*After indicated cycle, mold cooled to room temperature to prevent sticking.



Photograph 50  
Test Ablative Nose Cones  
Reinforced with Glass Flake-Impregnated Polyester Resin

**TABLE 68**  
**Formulations & Curing Variables for Glass Flake Reinforced Test Abutment Nose Cones**

	Photo 50 Epoxy Binder	Photo 50 Epoxy Binder	Photo 50 Polyester Binder
Molding Temperature, °F.	200	200	200
Mold Pressure, psi	800	1200	400
Molding Time, Minutes	60	60	20
Postcure: Time, Hrs.	2	2	-
Temperature, °F.	400	400	-
Formulation: Parts			
Jones Dabney Epi-Res 509	100	100	-
Methyl Nadic Anhydride	95	95	-
DMP-10 (Rohm & Haas)	2	2	-
American Cyanamid Laminac 4128	-	-	100
Benzoyl Peroxide	-	-	2
Glass Flake Content, Wt. %	50	70	50
Resin Content, Wt. %	50	30	50



As noted earlier in this report, Phase II work was continued during progression of Phase III. Since good results had been obtained with flat laminates from calendered sheet, a decision was made to attempt to use this material in the molding of a more complex part.

B-staged oriented (calendered) epoxy-glass sheets were molded as follows: the flat rigid sheets cut into rectangles 2" x 4" were weighed and placed in a dielectric heater for 30 seconds. The warm pliable sheets were removed from the dielectric heater and bent to fit the female mold curvature. The mold was closed and cured as before.

The series of rocket exhaust nozzles were produced from glass flake reinforced premixes based on polyester and epoxy resins. Two glass flake contents, 50% and 70%, were chosen for these test moldings. Problems with uncontrolled resin flow yielded parts with visible flow, check or knit lines. The parts produced in the polyester resin based systems were of much poorer quality than the epoxy based parts. The epoxy units exhibited only one or two flow lines, otherwise, had generally acceptable visual quality. No processing difficulty was experienced and excellent orientation and mold contour was obtained. The individual molding parameters are presented in Table 69. Photograph 51 shows the nozzles.

It is believed that superior exhaust nozzles could be molded with glass flake premixes if a resin flow retardant such as asbestos were incorporated into the blend. The use of dielectrically heated, preoriented, calendered, B-stage sheets for compression molding of complex curved shapes was found to be practical. The two molded rocket exhaust nozzles molded from sheet material were (visually) superior to the molded units produced with bulk resin-flake systems. Flow lines and disorientation are minimized in the molded units. Ideally, the preweighed, dielectrically heated pliable sheet should be wrapped around the male plug.

Photograph 52 is a composite photograph of nine rocket exhaust nozzles.

#### V. 7. Electronic Gate

In Photograph 53, electronic gate assemblies fabricated by transfer molding glass flake reinforced premixes are pictured. Two resin binder systems, (polyester and epoxy) were used in the preparation of these parts. This part is used as a plug-in type device for a computer. Electronic components may be wired directly on the part giving it a flexibility equivalent to 3 or 4 different electronic functions. Commercially, diallyl phthalate is being used as the molding material.

**TABLE 62**  
**Molding Parameters - Rocket Exhaust Nozzle**

<u>System</u>	<u>Unit No.</u>	<u>Wt. of Premix g.</u>	<u>Cure Time Min.</u>	<u>Molding Pressure Tons</u>	<u>Cure Temp. °F.</u>	<u>Remarks</u>
50% Polyester	1	215	5	18	295	Short shot
50% Polyester	2	245	5	30	285	
70% Polyester	3	255	5	35	275	very dry part
50% Polyester	4	275	5	35	265	
50% Polyester	5	275	5	35	265	
50% Polyester	6	285	5	18	265	
50% Polyester	7	285	5	18	265	
50% Polyester	8	285	5	18	265	
50% Epoxy B-Stage*	9	295	24	18	265	Overcure
50% Epoxy B-Stage*	10	260	14	18	295	
50% Epoxy	11	275	20	15	295	No Flash on part
50% Epoxy	12	285	10	20	280	
50% Epoxy	13	285	10	20	280	
50% Epoxy	14	285	8"	20	280	
70% Epoxy	15	285	8"	20	280	Dry molding improved but resin dry with pure resin flashing
70% Epoxy	16	295	8"	70	280	

Press used - 190 Ton FEMCO 4.1" Ram

\*30 second preheat in dielectric heater

Epoxy System  
 Jones-Dabney Ep1-Res 505  
 Shell Curing Agent 2

Polyester System  
 Laminac 4128 American Cyanamid  
 Benzoyl Peroxide

100  
20

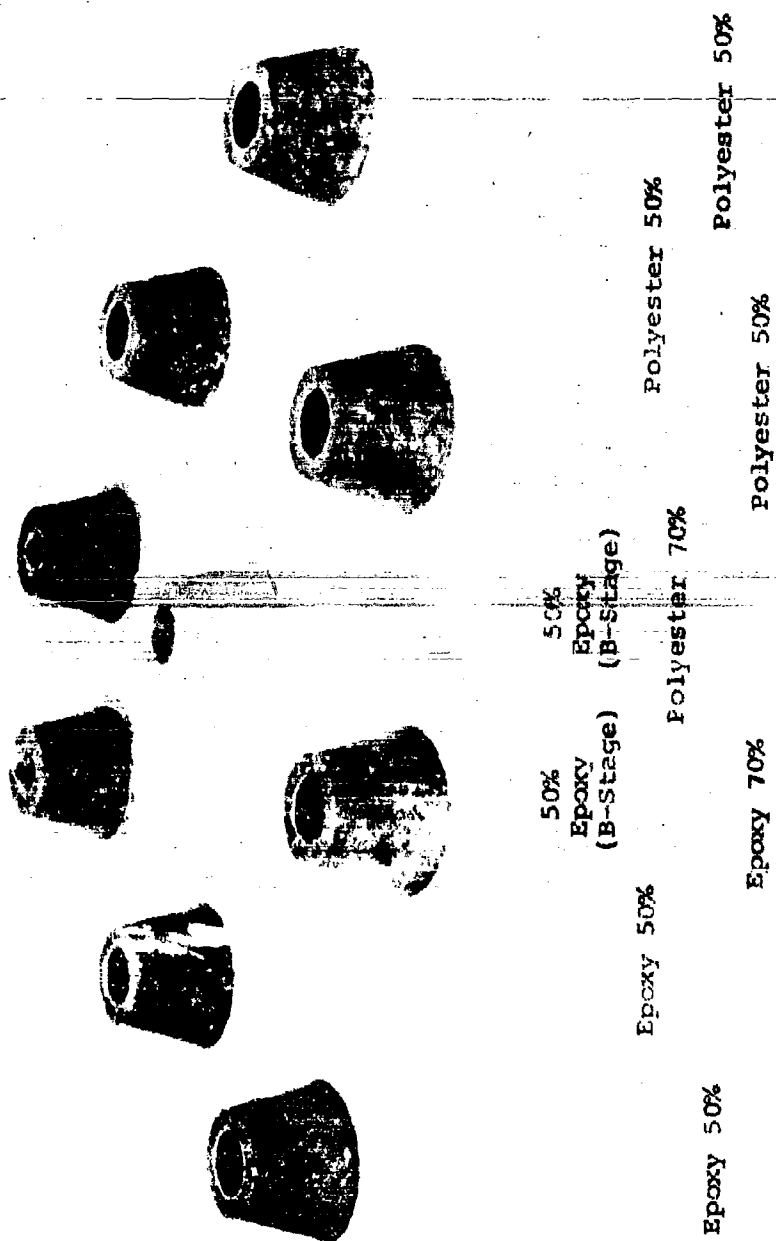
100  
25

Photograph 51

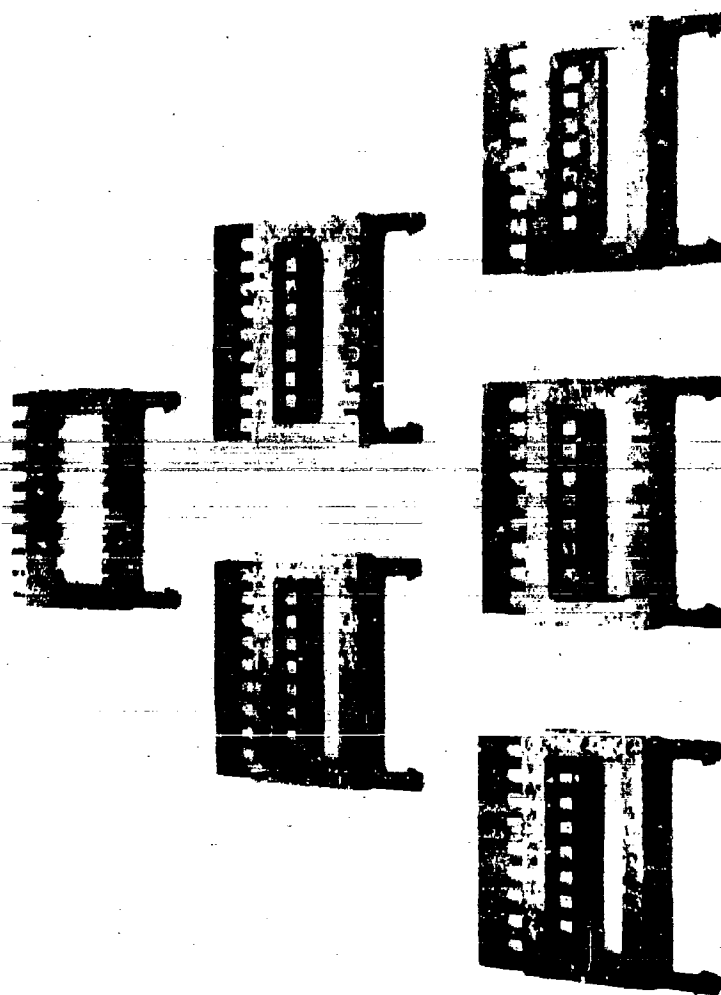


Rocket Exhaust Nozzles - Flashing in Place

Photograph 52



Composite of Molded Rocket Exhaust Nozzles



Photograph 37  
Electronic Gate Assemblies  
Glass Flake Reinforced Polyester and Epoxy Binder

A hand mold was used in fabrication of this part. The mold was constructed of three pieces; a transfer ram, and two matching cavity plates containing the cylindrical transfer pot. Fifty grams of the premix is charged into the cylindrical transfer pot. Thereafter, the transfer ram, a matched cylinder, having an outside diameter 3-4 thousandths less than the transfer pot, is inserted in the transfer pot above the charged material. The press is closed, exerting pressure on the transfer ram and material in the pot. The pressure "transfers" premix from the pot into the mold containing the cavity and metallic insert. After curing is complete, the mold is removed from the press, cooled, and disassembled to remove the part.

Table 70 contains curing and formulation data for the transfer molded gates. Photograph 53 shows six of the experimentally fabricated units molded from glass flake premixes.

#### V. 8. Electronic Bridge

The success experienced in molding the electronic gate assemblies led us to attempt molding a more complex electronic part. Again, transfer molding techniques were employed, this time using completely automatic presses and dielectrically heated preforms. The particular part was a 6" x 6" x 1/4" thick frame molded around 46 metallic pin type inserts as shown in Photograph 54.

The part on the left in Photograph 54 is "as molded" prior to removal of excess material from the center of the frame. The part on the right is the finished part. A preheated, preformed charge is molded perpendicular to the plane of the frame. The charge flows from the center of the mold into four large runners which are parallel to the plane of the frame shown in Photograph 54. The charge divided into four parts by the separators, flows through a 1/32" thickness gate - and forms the perimeter of the frame.

For this application an inert filled glass flake premix based on an epoxy resin was chosen because of flow and surface appearance requirements. A series of B-stage preforms 1-1/2" in diameter by 3/4" thickness were prepared for use in molding the part. These preforms were dielectrically preheated to 250°F. to provide required flow and shortened curing times. (A mineral filled phenolic is being used to mold this part commercially.)

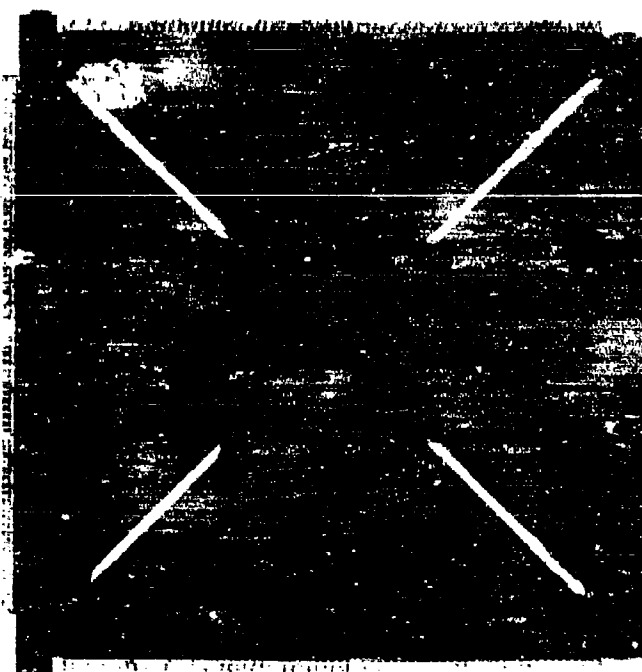
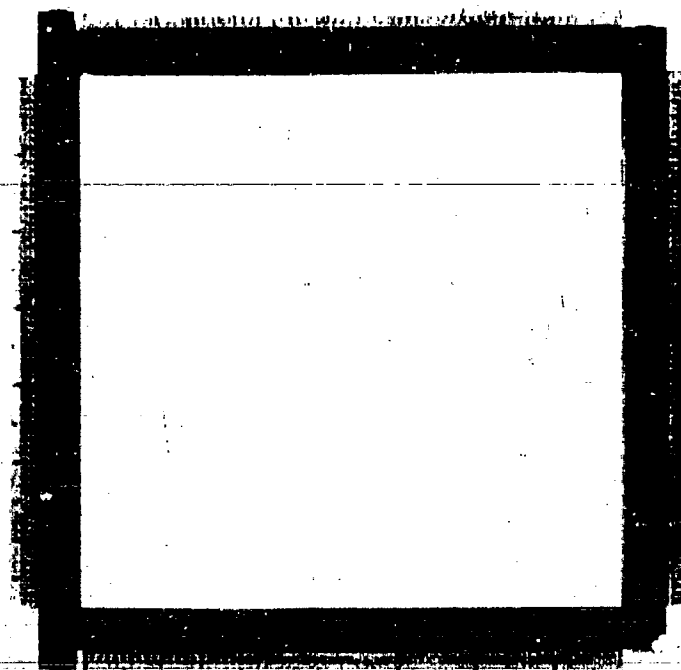
Complaints have arisen in the field because of part breakage. The flexural strength of the glass flake molding should exceed that of the mineral filled phenolic (11,000 psi).

Formulation data and curing parameters for this part appear in Table 71.

TABLE 70

Formulations & Curing Variables for Glass Flake  
Reinforced Transfer Molded Electronic Gates

	Epoxy Binder	Polyester Binder
Mold Temperature, °F.	200	200
Transfer Pressure, psi	4000	4000
Molding Time, Minutes	60	20
Postcure Time, Hrs.	2	-
Temperature, °F.	400	-
Formulation: Parts		
Jones-Dabney Epi-Res 509	100	-
Methyl Nadic Anhydride	95	-
DMP-10 (Rohm & Haas)	2	-
American Cyanamid Laminic 4128	-	100
Benzoyl Peroxide	-	2
Glass Flake Content, Wt. %	50	50
Resin Content, Wt. %	50	50



Photograph 54  
Transfer Molded Electronic Frame Containing Metallic Inserts



Table 71Formulations & Molding Variables - Electronic Bridge

Preheat Time, Seconds	30
Preform Temperature, °F.	250
Mold Temperature, °F.	280
Mold Clamp Pressure, Tons	70
Transfer Pressure, psi	300-500
Mold Time, Minutes	6-15
Formulation: Parts	
Jones-Dabney Epi-Res 510	75
Jones-Dabney Epi-Res 504	25
Shell Curing Agent Z	20
Fillers:	
Glass Flake, Wt. %	25
Asbestos 7TF	10
Surrex-MM Calcium Carbonate	20
Clinco Black Epoxy Paste	2
Resin Content, Wt. %	43

## Note:

Molding equipment: Stokes model 727-1 automatic transfer mold, press

Preheater - 3 1/2 kw "Thermal" dielectric preheater

Mold reproduction of the glass flake premix filled with "inerts" was excellent. Surface gloss was identical to the phenolic molded parts. Delamination was noted around the metallic inserts at the four corners of the part. This was due to slight sticking of the part during ejection from the press, as a result of minimizing curing times in the mold. Parts were produced at curing times of 6 and 8 minutes. Parts cured at 15 minutes - 1/2 hour, normal for the epoxy formulation, should have exhibited improved quality.

The physical properties of the glass flake reinforced premix used to mold the multi-insert electronic bridge frame were determined on a flat laminate molded at Olin. These properties are presented in Table 72. The flat laminate was molded in the 7" x 7" mold using the following conditions: temperature, 250°F; pressure, 2500 psi; time, one hour. No dielectric preheating was used prior to compression molding in the Watson-Stillman press. The resin was B-staged overnight and stored in a dry ice chest prior to molding.

#### V. 9. Conclusions

Phase III of the subject contract required the fabrication of at least six complex configurations from glass flake premixes using the most applicable fabrication method as determined from our previous studies in Phase II-A and II-B.

Subcontracted work of Phase III of the contract was completed upon the successful molding of rocket exhaust nozzles by the subcontractor. The units were molded in 50% and 70% glass concentrations in both a polyester and epoxy based premix system. The 70% content system produced parts which exhibited resin starved areas.

The configurations molded at subcontracted facilities included: missile stabilizer fin, practice nose cone, ablative test nose cone, windshield insert, electronic gate assembly, electronic frame and rocket exhaust cone.

Photographs 55 and 56 are composites of the simple and complex shapes which have been molded under this contract. Table 73 lists all the complex shapes molded, the molding process and resin systems used.

The compression and transfer molding of glass flake premixes performed in this phase of the program have exhibited excellent moldability. The parts were not optimum since time was not taken to optimize formulation to the design and production curing cycles. There is indicated by the results of these studies that a potential for glass flake premixes as a molding material does exist. It is important to consider this material when parts are required to have exceptional properties as well as good strength.

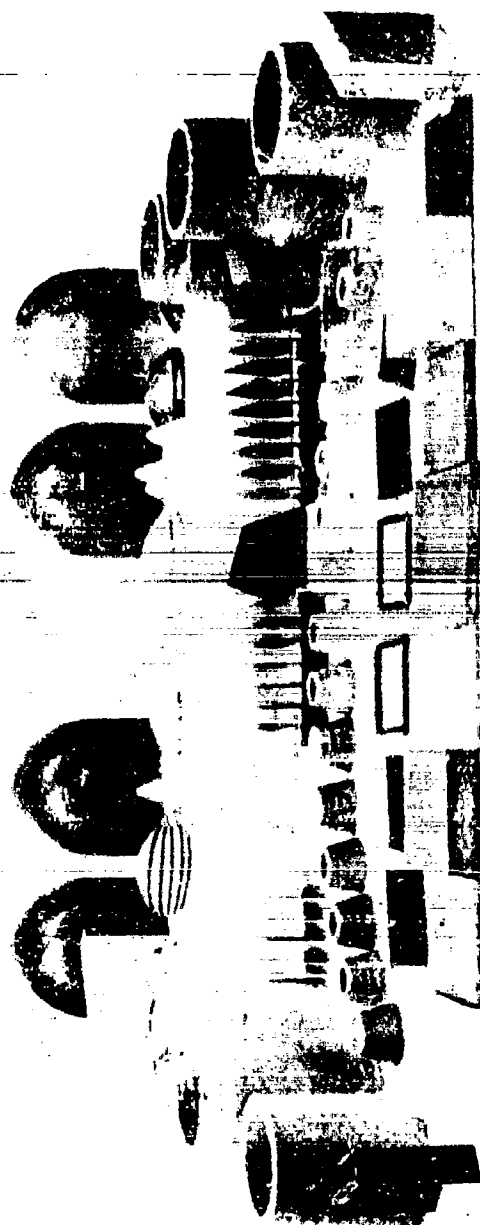
Table 72

Properties of Resin Used In Multi-Insert  
Electronic Bridge

Izod Impact, Ft. Lbs./In. Notch	0.28
Tensile Strength	
a. Strength, psi x 10 <sup>3</sup>	8.2
b. Elongation, %	.56
c. Modulus, psi x 10 <sup>6</sup>	1.55
Flexural Strength	
a. Strength, psi x 10 <sup>3</sup>	14.7
b. Modulus, psi x 10 <sup>5</sup>	9.41
Compression	
a. Strength, psi x 10 <sup>4</sup>	2.64
b. Modulus, psi x 10 <sup>5</sup>	7.43



Photograph 55  
Assembly of Molded Parts Glass Flake Reinforced



Photograph 56  
Composite of Simple and Complex Molded Shapes

**Table 73**  
**Complex Shapes Molded Under the Contract**

	1			2			3		
	Resin	% Glass	State	Resin	% Glass	State	Resin	% Glass	State
1. Missile Fin	Epoxy	50	B staged Premix	Epoxy	70	B staged Premix	Polyester	70	Wet Premix
2. Practice Nose Cone	Epoxy	50	Wet Premix	Epoxy	65	Wet Premix	Epoxy (CaCO <sub>3</sub> Filled)	40	Wet Premix
3. Ablative Teat Nose Cone	Epoxy	50	Wet Premix	Epoxy	70	Wet Premix	Polyester	50	Wet Premix
4. Windshield Insert	Polyester (Filler CaCO <sub>3</sub> )	50	Wet Premix	Epoxy	50	Wet Premix	Silicone	50	Wet Premix
"	Polyester (Asbestos filler)	25	Wet Premix	CaCO <sub>3</sub> Epoxy Asbestos	25	Wet Premix			Wet Premix
5. Electronic Gate Assy.	Epoxy	50	Wet Premix	Polyester	50	Wet Premix			Wet Premix
6. Electronic Frame	Epoxy	25	Wet Premix	Fillers CaCO <sub>3</sub> Asbestos Black Epoxy Paste					Transfer Molded
7. Rocket Exhaust Cone	Epoxy	50		Epoxy	70		Polyester	50	Transfer Molded
"	Polyester	70							

The major drawbacks encountered in molding were excessive resin flow and disorientation of flakes. Both of these defects can be overcome by tailored compounding of the premix formulation. Table 74 compares the strength of various commercially available premix materials. It can be seen that glass flake premixes compare favorably with most of the representative premix systems listed.

Laminates reinforced with glass flake have been prepared with a variety of resin systems. The epoxy resin laminates have shown the highest strengths, but properties have not equalled target values of:

- |                         |            |
|-------------------------|------------|
| 1. Compression strength | 55,000 psi |
| 2. Flexural strength    | 45,000 psi |
| 3. Tensile strength     | 25,000 psi |

Thin, flat laminates of controlled flake orientation prepared by the two developed mixing methods have shown properties in the range of target values.

In all cases where thicker laminates of complex molded shapes have been prepared, using wet premixes or B-staged preforms of wet premixes, a degraded laminate strength has resulted. This phenomenon is due to the uncontrollable flow of premix material within the mold of any complex shape. During flow of the premix in the mold, turbulent flow takes place, disrupting the parallel orientation of the glass flake. Without glass flake parallel orientation, strength properties are known to be degraded. It has been reported that unoriented premix moldings with epoxy binder have tensile and flexural strengths one-third of the tensile and flexural strengths of oriented material.

These results emphasize that glass flake reinforced plastics should not be considered as a replacement for glass cloth or fiber reinforced composites. The tensile and flexural strength of flake moldings tested are only approximately 1/2 of the corresponding glass cloth reinforced tensile and flexural strengths.

The glass flake reinforced plastics should be considered as a premix molding compound for the production of compression and transfer molded parts for missile and aircraft hardware. Our studies illustrate that the premixes have excellent flow characteristics in complex molds, such as the missile stabilizing fin. As a premix molding compound, glass flake reinforced plastics have physical properties which can be favorably compared with characteristics of a great number of premix molding compounds. The physical properties of a variety of premix compounds that have been used or screened for use in production of compression or transfer molded missile hardware were listed in Table 74. The advantage in flexural modulus gained by using glass flake reinforced plastics should be noted as one of the outstanding characteristics of glass flake reinforced composites. The tensile modulus of glass flake composites is also higher than almost all premix molding compounds regardless of filler type.

It should be noted that two of the glass flake moldings chosen for Table 74 represent maximum strengths obtainable for moldings prepared from Abbe, C. wet mixing, premixes and for moldings prepared from dry blended premixes.

TABLE 14  
COMPARATIVE STRENGTH DATA FOR PREPREG MOLDING COMPOUNDS\*  
AND GLASS FIBER REINFORCED PLASTIC MOLDINGS

Prepreg Compound	Resin Binder	Tensile Strength	Modulus	Shear Strength	Compressive Strength
Glaskyd 2051	Alkyd	2410 psi	$1.1 \times 10^6$ psi	8,600 psi	16,200 psi
Glaskyd 2051B	Alkyd	-	$1.1 \times 10^6$ psi	10,300 psi	23,200 psi
Thermaflow 100	Polyester	6500	$1.3 \times 10^6$	13,200	23,400
Thermaflow 400	-	3800	$1.0 \times 10^6$	11,000	16,800
Thermaflow 800	-	3500	$1.0 \times 10^6$	10,200	19,200
Plaskon 446	Alkyd	5300	$1.4 \times 10^6$	12,150	27,500
Corde CS-1	Polyester	3300	$0.9 \times 10^6$	11,000	18,500
Corde CS-13	Polyester	1200	$0.8 \times 10^6$	9,900	21,200
Acme Diallyl Phthalate	Diallyl Phthalate	-	$0.6 \times 10^6$	12,000	22,000
Durez Diallyl Phthalate DC 1512	-	3000	$1.2 \times 10^6$	10,000	22,000
Corde Rovings	Epoxy	10,700	$2.0 \times 10^6$	16,000	26,000
Scotchply 1100	Epoxy	23,000	$2.5 \times 10^6$	21,000	36,000
Scotchply KC-123	Phenolic	-	$2.8 \times 10^6$	-	-
EMC 8237	Epoxy	7400	$1.3 \times 10^6$	10,000	27,700
Plaskon 540	Diallyl Phthalate	3700	$1.6 \times 10^6$	13,400	26,600
Fiberite #4032-2598	Phenolic	6300	$1.6 \times 10^6$	16,500	29,400
Durez 16771	Phenolic	-	$1.3 \times 10^6$	-	-
EL-23-4 70% Glass Flake	Epoxy-Acid Anhydride Cured Tensile Modulus $7.12 \times 10^6$ psi	19,100	$1.3 \times 10^6$	-	-
EL-26-1 70% Glass Flake	Epoxy-Amine Cured	18,200	$0.6 \times 10^6$	-	14,360 <sup>6</sup> $1.01 \times 10^6$ psi modulus
Molded Part 70% Glass Flake	Epoxy-Amine Cured	5420 <sup>6</sup> $1.7 \times 10^6$ modulus	$1.1 \times 10^6$	-	-

Parallel orientation glass flake in flat sheet. Prepared by Abbe mixing.

Parallel orientation glass flake in flat sheet. Prepared by dry blending.

Molded complex parts  
Missile fin

\* Information obtained from Raychem's Plastics Plant in Hayward, Massachusetts. For listed materials with exception of glass flake moldings. All data collected for 5 x 5 flat sheets, compression molded by Raychem, glass flake moldings 7 x 7 or 10 x 10 compression moldings.



As discussed in the report, complex molded shapes reinforced with glass flake, such as the missile fin, do not possess the strengths of the same material in simple flat sheets. This reduction in strength in complex shaped pieces is common with other reinforced plastics systems.

## APPENDIX A

### Use of Inert Fillers Combined with Glass Flake Premixes

It has been apparent that the glass flake laminates will exhibit optimum physical properties only when the flakes are highly oriented and a minimum resin binder thickness has been obtained. Parallel flake alignment in a molded part even when preoriented B-staged preforms are used, will be difficult to obtain in all but simple flat or simple curved pieces. A substitute for the preoriented preforms desirable to the molding industry might be a molding powder or premix molding compound which could be used to mold any part. This material could result in considerable reduction in processing costs. In the cases where simple shapes of high strength would be required, the process of molding preoriented sheets would be feasible but at higher cost.

#### 1. Experimental

Investigations were made of the use of inert fillers with glass flake as a method of reducing the cost of the molding compound yet retaining physical properties. The use of these fillers is widespread throughout the reinforced plastics industry for three major reasons:

- (a) lower cost of molding compounds by virtue of reducing glass and resin requirements;
- (b) retention of the strength of a molded part at the same time lowering glass content; and
- (c) production of molded parts with improved surface, appearance and texture, and increased shrinkage resistance in the mold.

Compression molding of formulations prepared with calcium carbonate, (Surfex min-Diamond Chemical Company) and titanium dioxide (National Lead Company) had an excellent molded appearance. Tensile values were obtained for both sheets. (Average values are presented in Table A1.) Tensile values for a 40% glass content with fillers are higher than the values for other laminates prepared from Abk premixes containing only 40% glass. These results show the feasibility of using a pigment filled glass flake molding formulation for a general purpose or premix molding compound where very high material strength would not be a critical requirement, e.g., heater ducts for aircraft. The material has a stiffness advantage, in that its tensile modulus is equivalent to other fiber glass reinforced polyesters and epoxy laminates containing the same or slightly higher glass content.

#### 2. Conclusions

The use of fillers is feasible and produces premixed glass flake materials suitable for use as commercial filled resin premixed systems. The development of this phase of the glass flake "art" will be as difficult as the development of other epoxy and polyester premixed systems. The number of potential inert or reinforcing fillers is great and the effect of each one or combinations of fillers upon physical properties will have to be determined if the material is to be successfully used commercially.

**TABLE A1**  
**Tensile Properties for Inert Filled**  
**Glass Flake - Epoxy Laminates**

Inert Filler	Filler Content %	Glass Content %	Resin Content %	Laminate Size inches	Average Strength ksi	Tensile Modulus psi
Titanium Dioxide	20	40	40	9x9x0.147	7420	2.32x10 <sup>6</sup>
Calcium Carbonate	24	40	36	9x9x0.135	4890	2.35x10 <sup>6</sup>

**Preparation and Curing Data**

Inert Filler	Resin Formulation-Parts by Weight	Mixing	Press		Oven	
			Time hrs.	Temp. °F.	Pres. psi	Time hrs. Temp. °F.
Titanium Dioxide	Jones Dabney Epi-Rez 509-100 plus Methyl Padiac Anhydride 90 plus DMP - 10 15	Ross Mixer 25 mins	1	200	500	2 350
Calcium Carbonate			1	200	900	2 350

APPENDIX BTough Plastic-Glass Flake Laminate

The objective of this study was to combine Olin's tough plastic resin system with glass flake in an attempt to incorporate the observed high impact strength characteristics of tough plastic formulations with high tensile strengths of glass reinforcement.

1. Experimental

During the mixing of the highly viscous resin with the glass flake, poor flake wet-out was encountered. Although a 50 per cent resin binder was used, the high viscosity of the resin system produced a mixing similar to the mixing action encountered when processing a 70/30 glass fluid epoxy resin mixture. After a 20 minute mixing time in a Ross laboratory mixer, the glass flake appeared almost uncoated. The molded 9 x 9 sheet, however, had an acceptable appearance and tensile and impact strength values which are shown in Table B1. The values were slightly higher than those obtained with unfilled Tough Plastic.

Laminates containing 70 per cent glass flake should yield higher strength and modulus values than can be realized with the 50 per cent glass flake mixtures. The 50 per cent glass flake mixture laminates did not show significant increases in physical properties. If the anticipated high tensile and impact strength values could be realized with the 70 per cent glass flake content laminates, it may be worthy of consideration as a material of construction for recoverable experimental rocket nose cones.

**TABLE B1**  
**Average Tensile & Impact Strengths of Tough Plastic**  
**& Glass Flake Filled Tough Plastic Laminates**

	Average Tensile Strength	Average Impact Strength
Unfilled Tough Plastic	1800 psi	2.0 ft-lbs/in. notch
50% Glass Flake Filled	2200 psi	2.8 ft-lbs/in. notch

Resin Formulation	Mixing	Curing
Proprietary Formulation	Ross Mixer 1/2 hr.	Overnight to "B"-stage 1 hr. at 266°F. 20 mins. at 365°F.

## APPENDIX C

### Description of Test Methods

#### 1. Tensile Properties of Plastics

##### a. Scope

The test used was in accordance with Federal Specification Method LP 406 m1011 (ASTM D638-58T). This method is intended for use in determining the comparative tensile properties of plastics in the form of test specimens of standard shape tested under defined conditions.

##### b. Apparatus

Testing was performed on a Tinius Olsen Plastiversal machine with a 20,000 lb. capacity, equipped with a type U-1 and S-2 Tinius Olsen strain instrument and recorder.

##### c. Test Specimens

Test specimens for this tensile test were cut with a band saw from the 9 x 9 or 7 x 7 inch cured laminated sheets. Originally, the dimensions of the tensile strips cut from the cured laminated sheets were 3/4" in width x 9" total length. The 3/4 x 9 inch strips were then machined into the required ASTM shape using a "tensile-kut" machine equipped with a diamond plated cutter. During earlier tensile testing, it was noticed that the tensile strips were not failing within the prescribed gauge length of the specimen. Thereafter, the sample width was increased from 3/4" to 1". At this time, the 1" wide sample strip appears to be giving satisfactory results inside the gauge length breakages.

##### d. Procedure

As dictated in the specification method, the rate of head travel of the testing machine was .05 inches per minute during the entire test. During the test, elongation of the sample was measured with the type U-1 Tinius Olsen strain instrument and recorder. All specimens were tested in the direction perpendicular to molding pressure and parallel to flake direction.

##### e. Calculations

The tensile strength of the sample was calculated by dividing the maximum or breaking load in pounds by the original minimum cross sectional area of the specimen in square inches. The tensile elastic modulus was calculated by producing the initial linear portion of the stress-strain curve, selecting any point on the straight line thus drawn, and dividing the tensile stress (nominal) represented by the point by the corresponding strain at the same point.

## 2. Flexural Properties of Plastics (ASTM D790-48T) (LP 406B, m1031)

### a. Scope

This method was performed in accordance with Federal Specification LP 406B, m1031 (ASTM D790-48T). This method covers the procedure for determining the flexural properties of rigid plastic materials.

### b. Apparatus

The Tinius Olsen Elastiversal machine and a Tinius Olsen ASTM Standard Flexural Test Jig were used for these tests. The type U-1 Tinius Olsen Strain instrument was used to record the load deflection curve of the sample during testing.

### c. Procedure

The rate of head travel of the testing machine under load was not greater than .05 inches per minute during the test. A Tinius Olsen U-1 extensometer was used to measure deflection of the sample during testing. All specimens were tested in this direction perpendicular to flake orientation, i.e., normal to the laminate surface.

### Calculations

The flexural strength of the tested sample was calculated using the following formula:

$$S = \frac{3PL}{2BD^2}$$

where S = maximum fiber stress in pounds per square inch  
P = breaking load in pounds  
L = distance between support in inches  
B = width of beam tested in inches  
D = depth of beam tested in inches

### e. Modulus of Elasticity

The modulus of elasticity of material tested was calculated from the following formula:

$$E_B = \frac{L^3}{4BD^3} \frac{(P)}{Y}$$

where  $E_B$  = modulus of elasticity in bending,  
pounds per square inch  
L = distance between points of support, inches  
B = width of beam tested, inches  
D = depth of beam tested, inches  
 $\frac{P}{Y}$  = slope of initial straight line portion of  
load curve, pounds per inch deflection

### 3. Compressive Properties of Plastics

#### a. Scope

This test was performed in accordance with Federal Specification LP 406b, m1021 (ASTM D695-56).

This method provides procedures for the determination of the mechanical properties of rigid plastics when loaded in compression at relatively low uniform rates of straining or loading.

#### b. Apparatus

The 20,000 lb. capacity Tinius Olsen Plastiversal machine was used with a Tinius Olsen standard ASTM compression testing jig. The U-1, separable extensometer, was used to measure deflection of the sample during compression loading.

#### c. Test Specimens

For these samples, specimens 1 x 1 inch x the sample thickness were cut from the laminate sheet with a band saw and then finished on the "Tensil-kut" machine to assure parallelism of all edges. These same 1 x 1 inch x sample width thickness samples were used in a non-standard edgewise testing procedure. The 1 x 1 inch sample was chosen because the compression test jig did not allow for vertical support of these samples during testing. The use of a standard compression sample would not permit compression loading of the sample without bending.

#### d. Procedure

In accordance with the test method, the cross head speed was .05 inches per minute. Specimens were tested perpendicular to the plane of molding pressure and parallel to flake direction.

#### e. Calculations

The compressive strength was calculated by dividing the maximum compressive load carried by the specimen during the test by the original cross sectional area of the specimen. The elastic modulus was calculated by drawing a tangent to the initial linear portion of the stress-strain curve, selecting any point on the straight line, and dividing by the compressive stress (nominal) represented by the point by the corresponding compressive strain represented by the same point.

### 4. Standard Deviations

The standard deviations of test results were calculated using the following formula:

$$\sigma = \sqrt{\frac{x^2 - n\bar{x}^2}{n-1}}$$

where  $\sigma$  = standard deviation  
 $x$  = value of a single observation  
 $\bar{x}$  = arithmetic mean of a set of observations  
 $n$  = number of samples tested



## 5. Izod Impact Properties of Plastics

### a. Scope

This method is designed for use in determining the relative susceptibility of plastics to fracture by shock as indicated by the energy expended by a standard pendulum-type impact machine in breaking a standard specimen in one blow.

### b. Apparatus

A Tinius Olsen Changeomatic Cantilever beam, pendulum-type impact tester was used for all testing.

### c. Test Specimens

Test specimens were cut from the original laminate by use of a band saw. These specimens were subsequently finished to a 1/2 inch x 2 1/2 inch x sample thickness using a belt sander. A 45° notch 0.10 inch deep was cut into the sample with a milling cutter. The notch was in the side of the molded sheet parallel to the direction of molding pressure.

### d. Procedure

In accordance with the specified test method, the sample is placed in a vise with the notch facing the pendulum. The pendulum, released from a fixed position, fractures the sample and records the amount of inch-pounds expended in the fracturing process.

### e. Calculations

The Izod impact values are calculated by dividing the value obtained from d. by 12 times the sample width, inches. This converts to a value of ft.-lbs. per inch notch

## 6. Determination of Glass Content in Cured Laminate

A 10-20 gram sample was cut from the original laminate and placed into a beaker containing approximately 80-90 mm. of fuming nitric acid. The resin was digested for a period of 16-24 hours on a steam bath. At that time, the remaining nitric acid and nitrated resin were decanted by vacuum through a sintered glass funnel. The acid wet glass flakes were then rinsed with distilled water several times. After it was apparent that traces of nitric acid and the nitro resin compounds had been washed free of the glass flakes, acetone was then used to remove water and residual resin. The sintered glass funnel and the wet glass flakes were then dried in an oven at 250°F. for a period of one hour. After this drying session, the glass funnel and flakes were weighed on an analytical balance. The glass content of the laminate was determined by dividing the original sample weight into final weight of the recovered glass flake. This method has been used for the epoxy binder system only. A modification is required when polyester resin binders are used. It now appears evident that the silicone resin binder system will have to be ashed in a muffle furnace for glass content determination.

## 7. Determination of Laminate Density ASTM LP 406B, m5011

### a. Scope

This method is designed for use in determining the specific gravity of solid plastics which are unaffected by water (short term exposure).

### b. Apparatus

An analytical balance with specific gravity bridge was used.

### c. Test Specimens

Specimens no larger than 1/2 inch x 1/2 inch x sample thickness were cut from the original laminate sheet and drilled for suspension in the specific gravity bridge.

### d. Procedure

The sample is weighed in air and then in distilled water at  $23^{\circ} \pm 1^{\circ}\text{C}$ .

### e. Calculations

The specific gravity of the sample is calculated from:

$$\text{Specific Gravity} = \frac{\text{weight in air}}{\text{weight in air} - \text{weight in water}}$$

TABLE C1

Flexural Test Dimension as a Function of Laminate Thickness

<u>Laminate Thickness</u> <u>Inches</u>	<u>Flexural Test Dimensions</u> <u>Inches</u>
3/8	1/2 x 8 (or 7 if 7 x 7 sheet used)
1/4	1/2 x 6
3/16	1/2 x 5
1/8	1 x 4

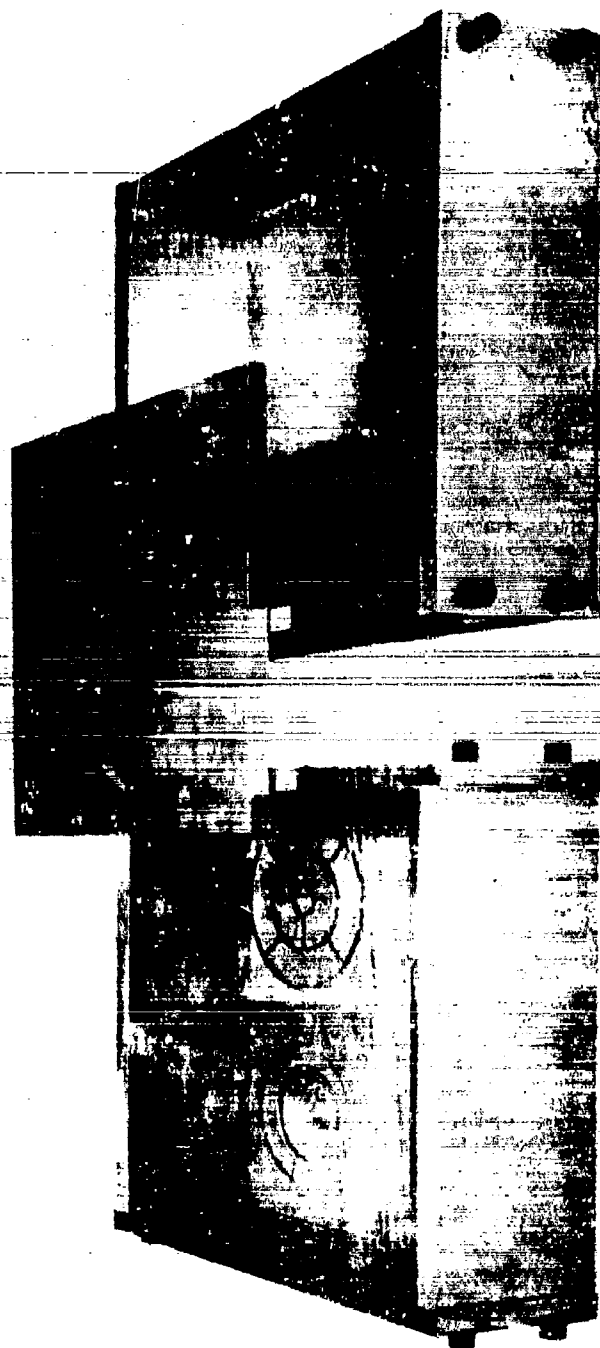
Any samples thicker than 3/8 inch are milled down to a 3/8 inch thickness before testing. An equal amount of material is taken off both sides of the laminate so that the 3/8 inch sample represents the middle of the test sample.



APPENDIX DEquipment Used in the Program

Equipment described in this report and used in the contract but not shown in the text of the report is shown here in Photographs D1-D8.

Photograph D1

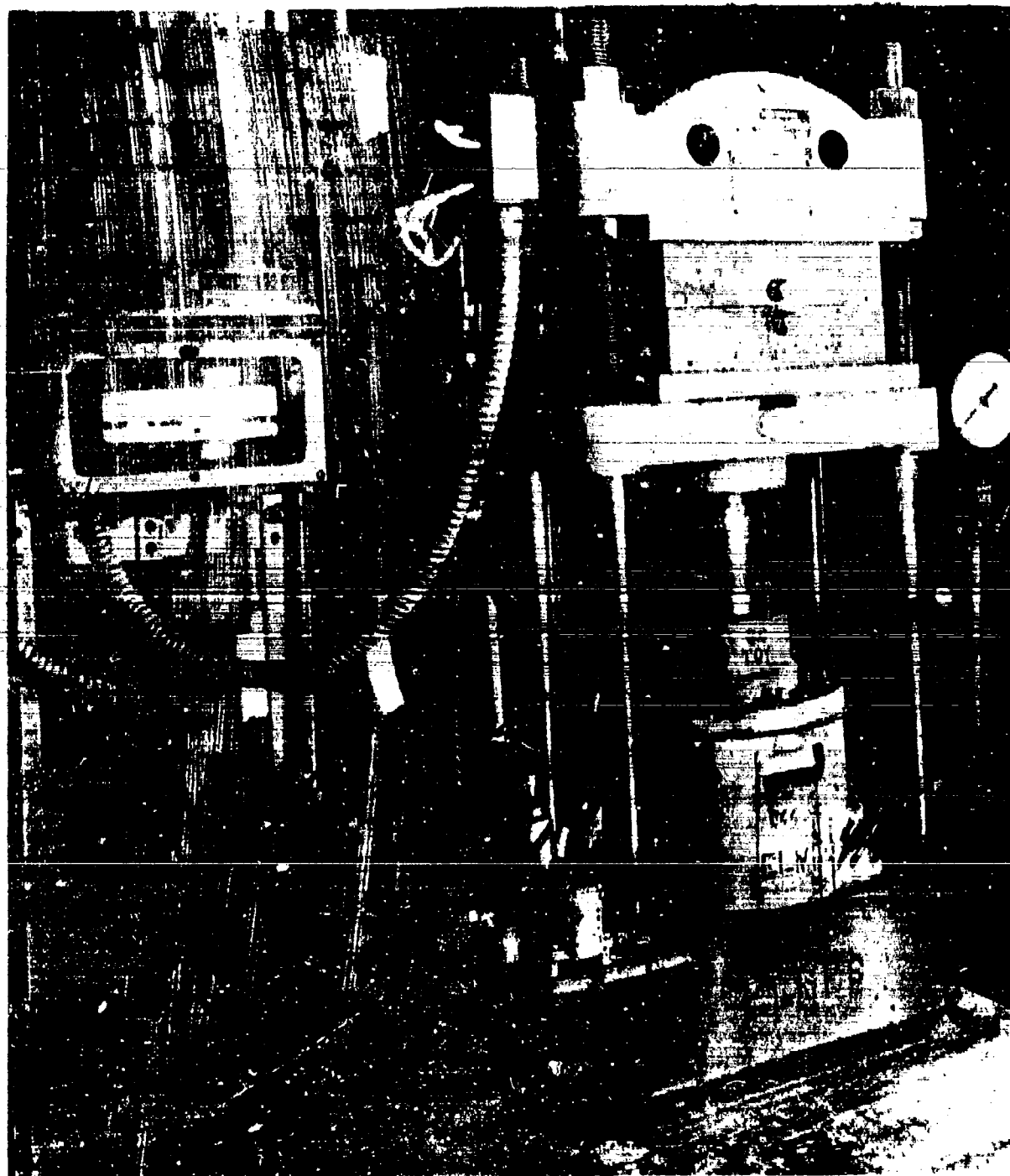


Simple Box Mold

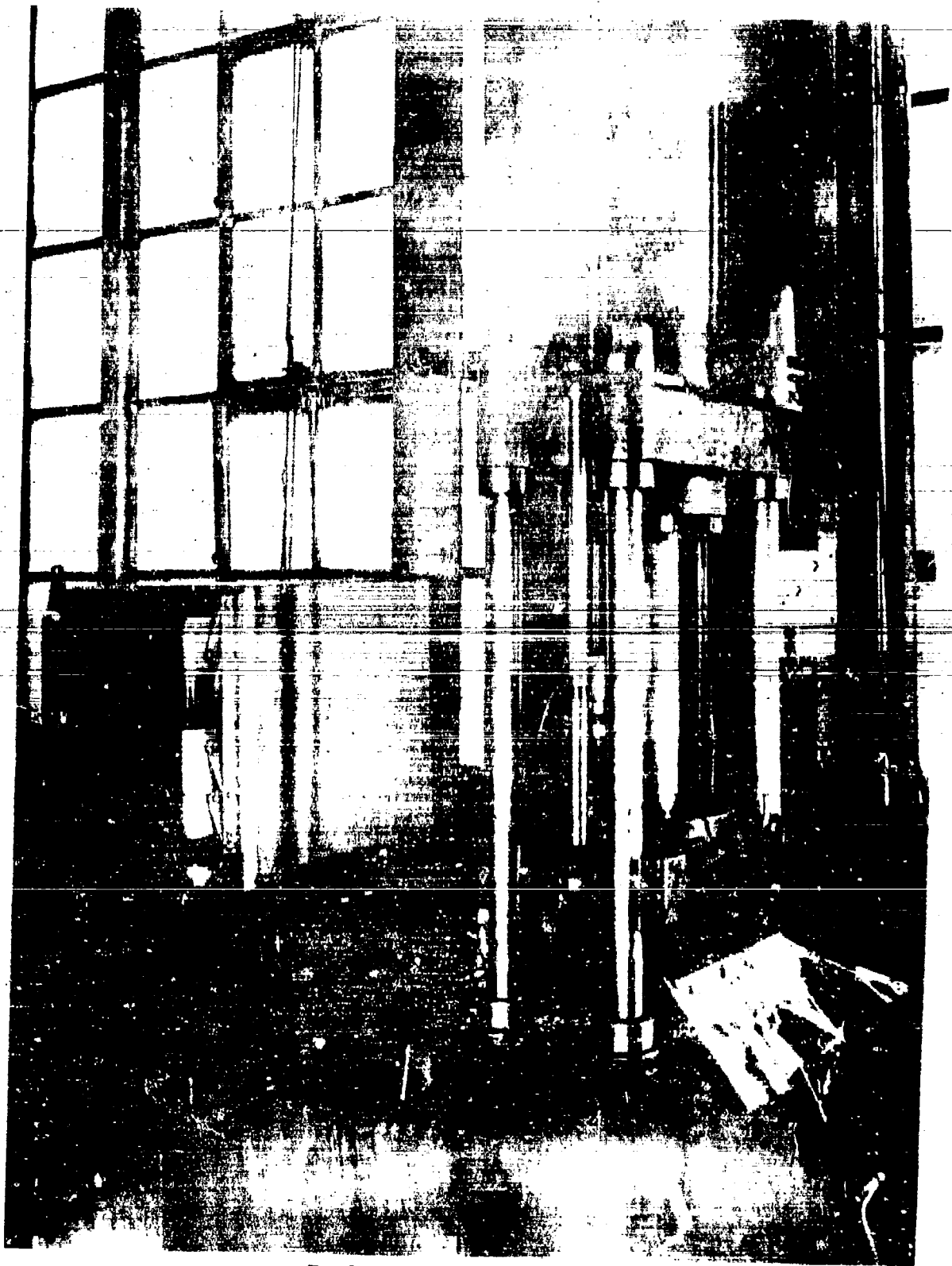
Planar Step Mold

9 x 9 Simple Box Molds Shown With  
Floating Top Plate

Photograph D2

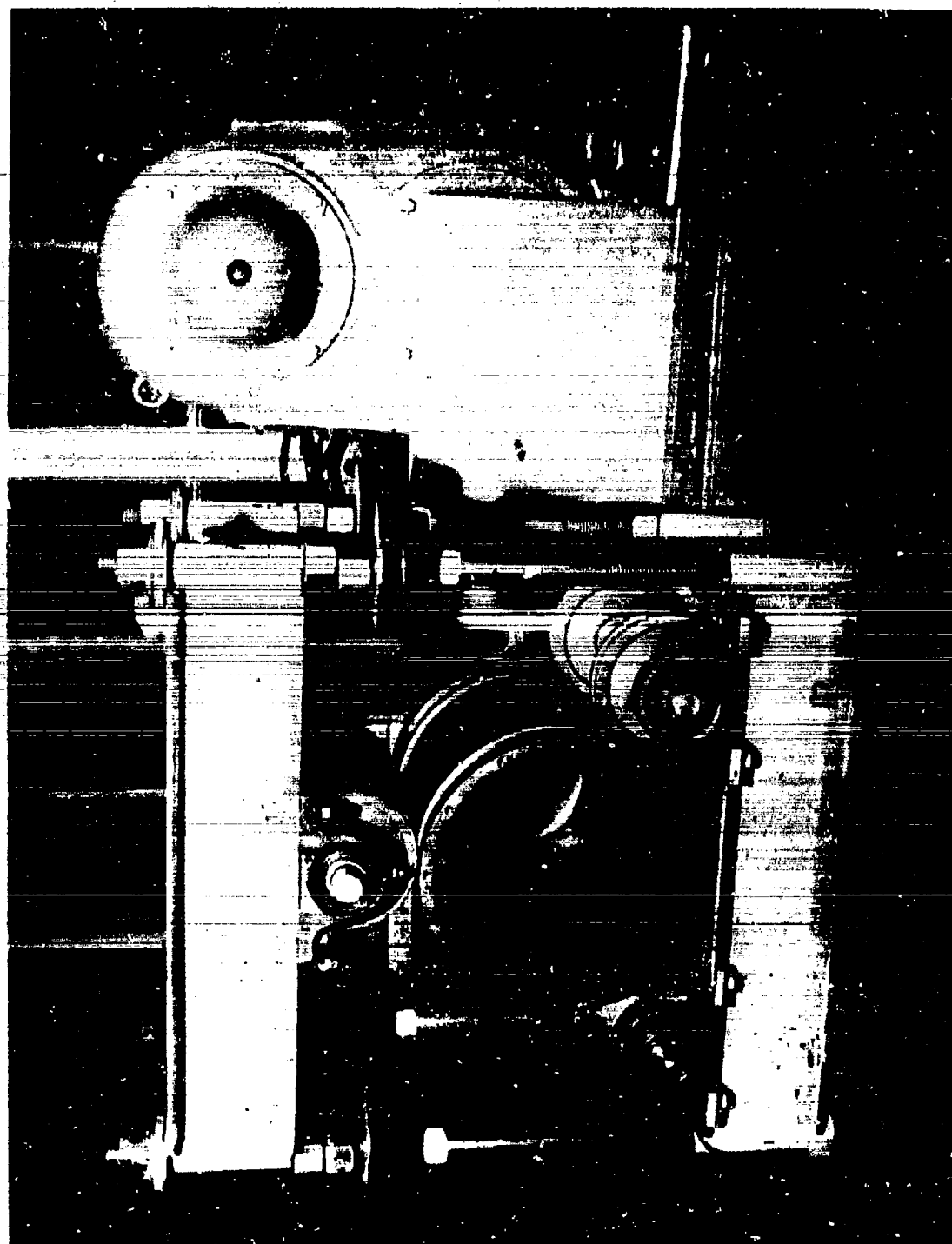


Ten by Ten Inch Elmes Hand Operated  
Compression Press (32 ton capacity)



Twelve by Twelve Inch Watson-Stillman  
Hydraulic Compression Press (45 ton capacity)

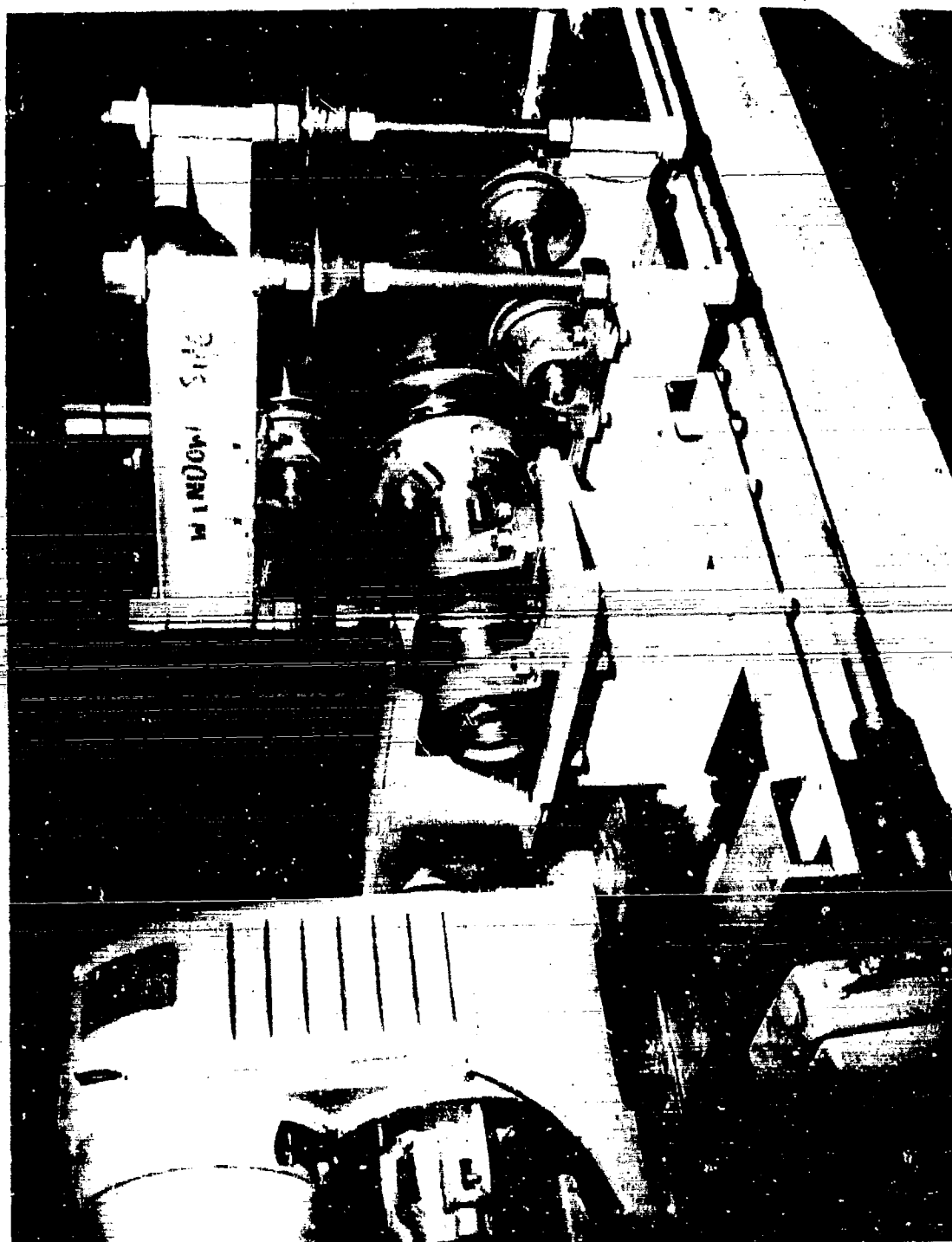
Photograph D



Horizontal Centrifuge Mold Chamber

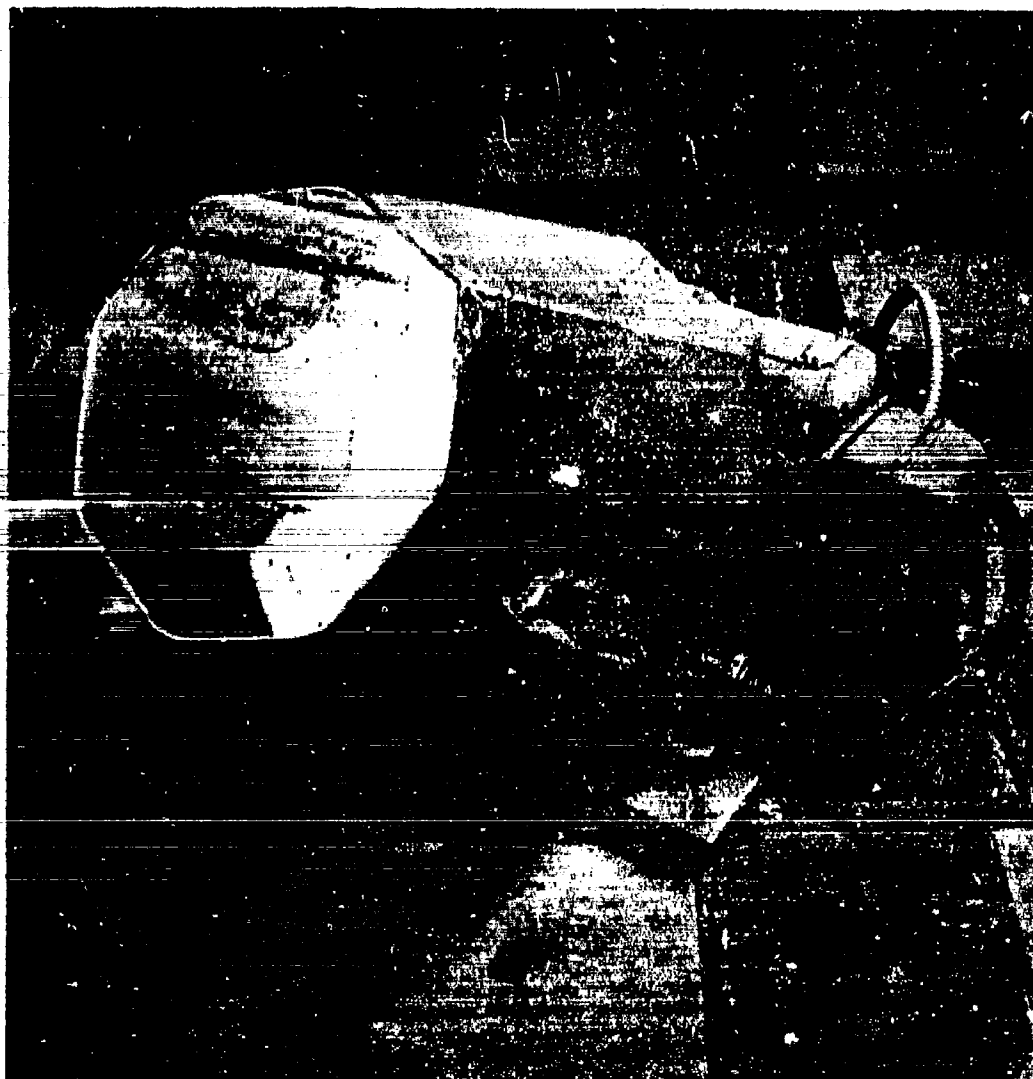


Photograph D5



Horizontal Centrifuge

Photograph D6



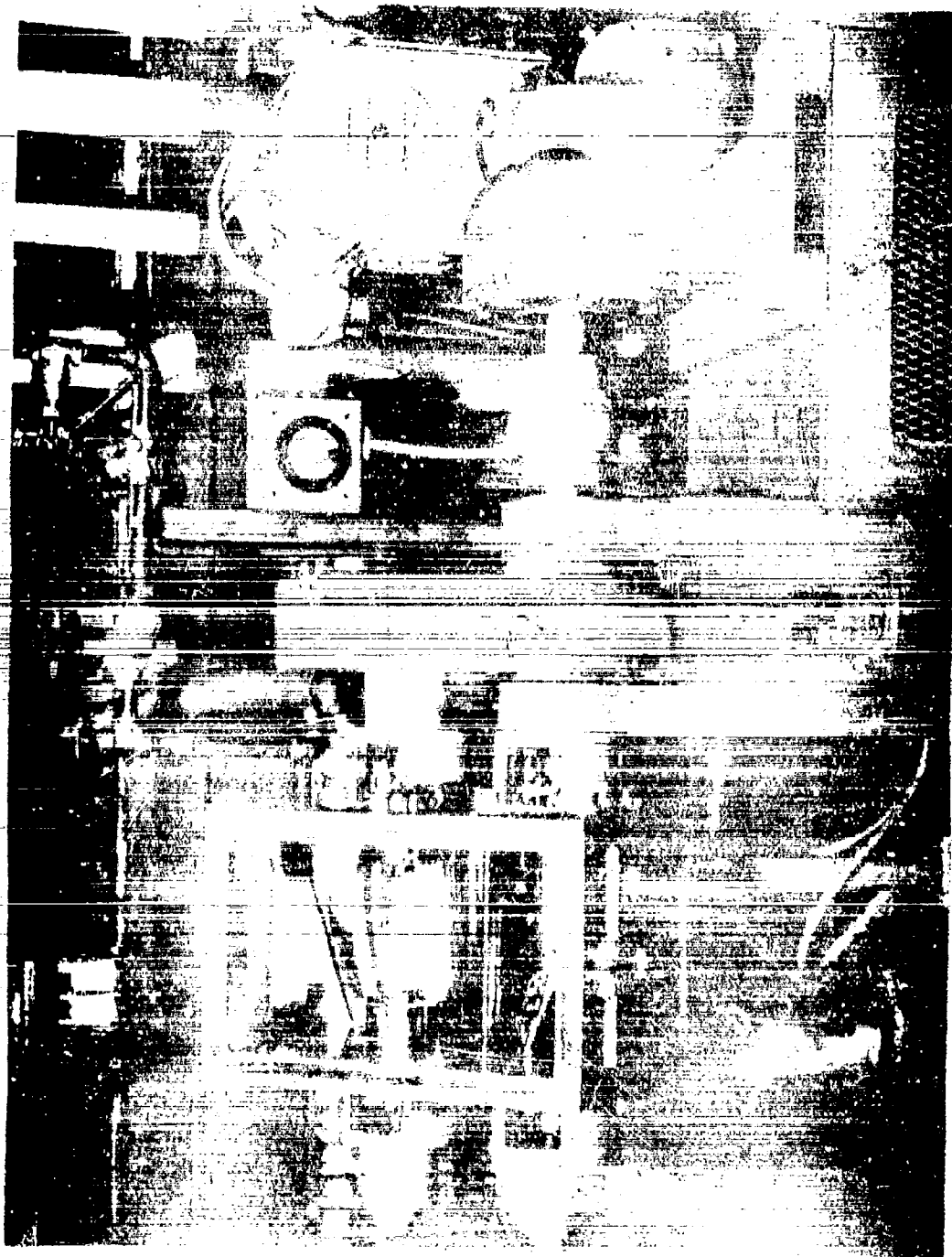
Glass Flake Tumbler  
(With a Glass Flake - Resin Blend Inside)

Photograph D7



7 x 7 Inch Compression Mold

Photograph D8



5 Gallon Abbe Mixer - Inside View

APPENDIX E

Listed herein are the various commercially available components of resin systems screened in the program to develop economic methods of manufacture for glass flake reinforced plastics.

Source of Compounds Used in Glastic

BF <sub>3</sub> - Ethylamine complex	Harshaw Chemical Co.
Ethylene diamine	Union Carbide Chem. Corp.
Diethylene triamine	"
Triethylene tetramine	"
Tetra ethylene pentamine	"
BLS 2680	"
Unox 201	"
Unox 206	"
Unox 207	"
Unox 269	"
ERLA 2255	"
ERLA 2256	"
ZZPA 0313	"
BLS 3021	"
BLS 2680	"
ERL 2794	"
ERRB 0100	"
BRP 5417	"
RLS 4587	"
BRP 5090	"
BRZ 7541	"
ERLA 2772	"
A-100 silane	"
ERRB 01001	"
1-2-6 Hexane triol	"
Hexahydrophthalic Anhydride	Allied Chemical Corp.
Phthalic Anhydride	"
Maleic Anhydride	"
Dodecenyl Succinic Anhydride	"
Methyl Nadic Anhydride	"
Meta phenylene diamine	"
Epon 820	Shell Chemical Co.
Epon 828	"
Epon 1031	"
Epon 1001	"
Epon 1007	"
Shell Z	"
6301 Epotuf	Reichold Chemical Co.
Epi Rez 502	Jones Dabney Co.
Epi Rez 504	"
Epi Rez 507	"
Epi Rez 509	"
Epi Rez 510	"
Epi Rez 520	"
Epi Rez 522	"
Epi Rez 540	"
Epi Rez 560	"

Epi Cure 87	Jones Dabney Co.
Epi Cure 854	"
Epi Cure 855	"
Epi Cure 852	"
4-4 Diamino phenyl sulfone	Polychemicals Labs, Inc.
Paraplex P-43	Rohm & Haas Co.
DMP-10	"
DMP-30	"
Dapon 35	Food Machinery & Chemical Co.
Emery Trimer Acid 3162D	Emery Industries, Inc.
Araldite 6005	Ciba Products Corp.
MR 37CX Polyester Resin	Celanese Corp.
Trimethylol propane	"
LP 3	Thiokol Chemical Corp.
EM 550	"
Het Anhydride	Hooker Chemical Co.
DEN 438	Dow Chemical Co.
Butadiene dioxide	Koppers Company
Silicone R 5581	Dow Corning Corp.
Silicone R 7521	"
Silicone R 5061	"
DC-7147	"
DC-7146	"
Dicumene peroxide R	Hercules Powder Co.
Pyromellitic Dianhydride	DuPont
Volan A	"
Benzoyl peroxide	Wallace & Tiernan Co.
tert-butyl peroxide	Matheson Co., Inc.
Methyl ethyl ketone peroxide	Cadet Chemical Corp.
R 14009 Phenolic	Monsanto Chemical Co.
Geon 121 (PVC)	Goodrich Chemical Co.
Omamid C-288	Olin Mathieson Chem. Corp.
Omamid T-590	"
Laminac Promotor 400	American Cyanamid Co.
Laminac 4128	"
Vibrin 1088-B	Neugatuck Chemical Co.
Vibrin 156	"
Toluene diamine	Olin Mathieson Chem. Corp.

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[illegible]

**OF DISPOSITION**

